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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/US92/04167 <b>(22) International Filing Date:</b> 19 May 1992 (19.05.92) <b>(30) Priority data:</b> 714,165 12 June 1991 (12.06.91) US 800,555 27 November 1991 (27.11.91) US 800,559 27 November 1991 (27.11.91) US <b>(60) Parent Application or Grant</b> <b>(63) Related by Continuation</b> 714,165 (CIP) US 12 June 1991 (12.06.91) Filed on <b>(71) Applicant (for all designated States except US):</b> UNIAX CORPORATION [US/US]; 5375 Overpass Road, Santa Barbara, CA 93111 (US). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only) :</b> CAO, Yong [CN/US]; 6739 El Collegio Road, Apt. 215, Goleta, CA 93117 (US). SMITH, Paul [NL/US]; 2318 Anacapa Street, Santa Barbara, CA 93105 (US). HEEGER, Alan, J. [US/US]; 1042 Las Alturas Road, Santa Barbara, CA 93103 (US).		<b>(74) Agent:</b> BENZ, William, H.; Morrison & Foerster, 545 Middlefield Road, Suite 200, Menlo Park, CA 94025 (US). <b>(81) Designated States:</b> AT, AT (European patent), AU, BB, BE (European patent), BF (OAPI patent), BG, BJ (OAPI patent), BR, CA, CF (OAPI patent), CG (OAPI patent), CH, CH (European patent), CI (OAPI patent), CM (OAPI patent), CS, DE, DE (European patent), DK, DK (European patent), ES, ES (European patent), FI, FR (European patent), GA (OAPI patent), GB, GB (European patent), GN (OAPI patent), GR (European patent), HU, IT (European patent), JP, KP, KR, LK, LU, LU (European patent), MC (European patent), MG, ML (OAPI patent), MN, MR (OAPI patent), MW, NL, NL (European patent), NO, PL, RO, RU, SD, SE, SE (European patent), SN (OAPI patent), TD (OAPI patent), TG (OAPI patent), US. <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> PROCESSIBLE FORMS OF ELECTRICALLY CONDUCTIVE POLYANILINE AND CONDUCTIVE PRODUCTS FORMED THEREFROM		
<b>(57) Abstract</b>  Compositions of electrically conductive substituted and unsubstituted polyanilines in nonconductive substrates such as polymers or polymer plus solvents with protonic acids are disclosed as are methods of forming such compositions and use of same to form conductive articles.		

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PROCESSIBLE FORMS OF  
ELECTRICALLY CONDUCTIVE POLYANILINE  
AND CONDUCTIVE PRODUCTS FORMED THEREFROM

## Background of the Invention

## 1. Field of the Invention

15 This invention relates to conductive polymers and particularly to the use of functionalized protonic acids to induce processibility of electrically conductive substituted or unsubstituted polyanilines, and to induce solubility of electrically conductive substituted or unsubstituted polyanilines in organic liquids and/or fluid (melt) phases of solid polymers. Other aspects of this invention relate to the resulting solutions of  
20 electrically conductive substituted or unsubstituted polyanilines in organic liquids, to solution-processing methods of forming such solutions and to methods of using such solutions to form conducting polymer articles. Yet other aspects relate to solid phase polymers containing  
25 these protonic acids and their use in conductive articles.

## 2. Prior Art

There has recently been an increased interest  
30 in the electrical conductivity and electrochemistry of  
polymeric systems. Recently, work has intensified with  
emphasis on polymers having extended conjugation in the  
backbone chain.

One conjugated polymer system currently under study is polyaniline. Kobayashi Tetsuhiko et al., J. Electroanal. Chem., "Electrochemical Reactions Concerned With electrochromism of Polyaniline Film-Coated Electrodes," 177 (1984) 281-291, describes various experiments in which spectroelectro-chemical measurement of a polyaniline film coated electrode were made. French Patent No. 1,519,729, French Patent of Addition 94,536; U.K. Patent No. 1,216,549; "Direct Current Conductivity of Polyaniline Sulfate," M. Donomedoff, F. Kautier-Cristojini, R. ReSur-vail, M. Jozefowicz, L.T. Yu, and R. Buvet, J. Chim. Phys. Physicochim. Brol., 68, 1055 (1971); "Continuous Current Conductivity of Macromolecular Materials," L.T. Yu, M. Jozefowicz, and R. Buvet, Chim. Macromol., 1, 469 (1970); "Polyaniline Based Filmogenic Organic Conductive Polymers," D. LaBarre and M. Jozefowicz, C.R. Read. Sci., Ser. C, 269, 964 (1969); "Recently Discovered Properties of Semiconducting Polymers," M. Jozefowicz, L.T. Yu, J. Perichon, and R. Buvet, J. Polym. Sci., Part C, 22, 1187 (1967); "Electrochemical Properties of Polyaniline Sulfates," F. Cristojini, R. De Surville, and M. Jozefowicz, Cr. Read. Sci., Ser. C, 268, 1346 (1979); "Electrochemical Cells Using Protolytic Organic Semiconductors," R. De Surville, M. Jozefowicz, L.T. Yu, J. Perichon, R. Buvet, Electrochem. Ditr. 13, 1451 (1968); "Oligomers and Polymers Produced by Oxidation of Aromatic Amines," R. De Surville, M. Jozefowicz, and R. Buvet, Ann. Chem. (Paris), 2, 5 (1967) "Experimental Study of the Direct Current Conductivity of Macromolecular Compound," L.T. Yu, M. Borredon, M. Jozefowicz, G. Belorgey, and R. Buvet, J. Polym. Sci. Polym. Symp., 16, 2931 (1967); "Conductivity and Chemical Properties of Oligomeric Polyaniline," M. Jozefowicz, L.T. Yu, G. Belorgey, and R.

- Buvet, J. Polym. Sci., Polym. Symp., 16, 2934 (1967); "Products of the Catalytic Oxidation of Aromatic Amines," R. De Surville, M. Jozefowicz, and R. Buvet, Ann. Chem. (Paris), 2, 149 (1967); "Conductivity and Chemical Composition of Macromolecular Semiconductors," Rev. Gen. Electr., 75 1014 (1966); "Relation Between the Chemical and Electrochemical Properties of Macromolecular Semiconductors," M. Jozefowicz and L.T. Yu, Rev. Gen. Electr., 75, 1008 (1966); "Preparation, Chemical Properties, and Electrical Conductivity of Poly-N-Alkyl Anilines in the Solid State," D. Muller and M. Jozefowicz, Bull. Soc. Chem. Fr., 4087 (1972).

- United States Patent Nos. 3,963,498 and 4,025,463 describe oligomeric polyanilines and substituted polyanilines having not more than 8 aniline repeat units which are described as being soluble in certain organic solvents and which are described as being useful in the formation of semiconductors compositions. European Patent No. 0017717 is an apparent improvement in the compositions of United States Patent Nos. 3,963,498 and 4,025,463 and states that the polyaniline can be formed into a latex composite through use of the oligomers of polyaniline and a suitable binder polymer.

- High molecular weight polyaniline has emerged as one of the more promising conducting polymers, because of its excellent chemical stability combined with respectable levels of electrical conductivity of the doped or protonated material. Processing of polyaniline high polymers into useful objects and devices, however, has been problematic. Melt processing is not possible, since the polymer decomposes at temperatures below a softening or melting point. In addition, major difficulties have been encountered in attempts to dissolve the high molecular weight polymer.

Recently, it was demonstrated that polyaniline, in either the conducting emeraldine salt form or the insulating emeraldine base form, can be processed from solution in certain strong acids to form useful articles (such as oriented fibers, tapes and the like). By solution processing from these strong acids, it is possible to form composites, or polyblends of polyaniline with other polymers (for example polyamides, aromatic polyamides (aramids), etc.) which are soluble in certain strong acids and thereby to make useful articles.

"Electrically Conductive Fibers of Polyaniline Spun from Solutions in Concentrated Sulfuric Acid," A. Andreatta, Y. Cao, J.C. Chiang, A.J. Heeger and P. Smith, Synth. Met., 26, 383 (1988); "X-Ray Diffraction of Polyaniline," Y. Moon, Y. Cao, P. Smith and A.J. Heeger, Polymer Communications, 30, 196 (1989); "Influence of the Chemical Polymerization Conditions on the Properties of Polyaniline," Y. Cao, A. Andreatta, A.J. Heeger and P. Smith, Polymer, 30, 2305 (1990); "Magnetic Susceptibility of Crystalline Polyaniline," C. Fite, Y. Cao and A.J. Heeger, Sol. State Commun., 70, 245 (1989); "Spectroscopy and Transient Photoconductivity of Partially Crystalline Polyaniline," S.D. Phillips, G. Yu, Y. Cao, and A.J. Heeger, Phys. Rev. B 39, 10702 (1989); "Spectroscopic Studies of Polyaniline in Solution and in the Solid State," Y. Cao and A.J. Heeger, Synth. Met. 32, 263, (1989); "Magnetic Susceptibility of One-Dimensional Chains in Solution," C. Fite, Y. Cao and A.J. Heeger, Solid State Commun., 73, 607 (1990); "Electrically Conductive Polyblend Fibers of Polyaniline and Poly(p-phenylene terephthalamide)," A. Andreatta, A.J. Heeger and P. Smith, Polymer Communications, 31, 275 (1990); "Polyaniline Processed From Sulfuric Acid and in Solution in Sulfuric Acid: Electrical, Optical and

Magnetic Properties," Y. Cao, P. Smith and A.J. Heeger in Conjugated Polymeric Materials: Opportunities in Electronics, Opto-electronics, and Molecular Electronics, ed. J.L. Bredas and R.R. Chance (Kluwer Academic Publishers, The Netherlands, 1990).

5 United States Patent No. 4,983,322 describes solutions and plasticized compositions of electrically conductive substituted and unsubstituted polyanilines and methods of forming such solutions or compositions and use  
10 of same to form conductive articles. The polyaniline materials were made soluble by the addition of an oxidizing agent such as  $\text{FeCl}_3$ . Since the resulting compounds are charge transfer salts, highly polar solvents were required; specifically solvents were needed  
15 with dielectric constants equal to or greater than 25 and with dipole moments equal to or greater than 3.25.

Starting with the insulating emeraldine base form, polyaniline can be rendered conducting through two independent doping routes:

- 20 (i) Oxidation either electrochemically (by means of an electrochemical charge transfer reaction) or chemically (by means of chemical reaction with an appropriate oxidizing agent such as  $\text{FeCl}_3$ );
- (ii) Protonation through acid-base chemistry by  
25 exposure to protonic acids (for example, in aqueous environment with pH less than 2-3). (1) 'Polyaniline': Protonic Acid Doping of the Emeraldine Form to the Metallic Regime by J.-C. Chiang and Alan G. MacDiarmid, Synthetic Metals **13** 193 (1986). (2) A Two-Dimensional-Surface 'State' Diagram for Polyaniline by W.R. Salaneck,  
30 I. Lundstrom, W.-S Huang and A.G. MacDiarmid, Synthetic Metals **13**, 297 (1986).

These two different routes lead to distinctly different final states. In (i), the oxidation causes a



change in the total number of  $\pi$ -electrons on the conjugated chain and thereby renders it conductive. In (ii), there is no change in the number of electrons; the material is rendered electrically conductive by  
5 protonation of the imine nitrogen sites.

In the general field of conducting polyaniline, it was believed impossible to dope a high molecular weight polyaniline to the extent that it becomes a semiconductor or conductor and thereafter dissolve or  
10 plasticize the conductive form of polyaniline in common nonpolar or weakly polar organic solvents. As used herein, the terms "to plasticize" and a "plasticized composition" refer to the process and product in which a solid polymer includes an admixed liquid or semisolid  
15 phase to an extent sufficient to render the solid polymer flexible (softened) and not brittle. The liquid or semisolid additive is known as a "plasticizer." The nature of plasticized materials is described in more detail in Harry R. Allcock and Frederick W. Lampe,  
20 Contemporary Polymer Chemistry, Prentice-Hall, Inc. Englewood Cliffs, N.J. (1981), p. 13.

In the absence of solutions or plasticized forms, comprising common nonpolar or weakly polar liquids, or otherwise processible forms, the ability to  
25 readily and economically form useful conductive articles out of conductive polyaniline, or composites or polyblends of conductive polyaniline with other polymers (for example polyethylene, polypropylene, polystyrene, elastomers, poly(ethylvinylacetate), etc.) is restricted.  
30 Thus, a need exists for techniques and materials to facilitate the fabrication of shaped conductive polyaniline articles, especially articles made from bulk material (conductive polyanilines and/or composites, or

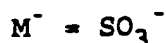
polyblends of conductive polyaniline with other polymers) and films, fibers and coatings.

In one aspect, this invention provides and the soluble conductive polyanilines provided lead to  
5 transparent conductive polymers. Prior art in this area includes Shacklette et al. (U.S. Patent No. 4,963,206, Oct. 16, 1990) applied a conductive polyaniline film onto Aclar by exposing the Aclar film to a mixture of aniline tosylate and ammonium persulfate in an aqueous solution  
10 of tosic acid. Thus the conductive polyaniline film was polymerized *in situ* onto the substrate. Fukunishi et al. (JP application no. 63145326, June 17, 1988) used similar techniques to prepare polymer composites by *in situ* polymerization of pyrrole and aniline. Takahashi et al.  
15 (JP application no. 63268733) prepared thin semitransparent films by electrolytic polymerization. Sakai et al. (JP application no. 63215772, Sept. 8, 1988) manufactured conductive polymer compositions by polymerizing monomers capable of forming anionic polymer  
20 electrolytes in the presence of polymers of  $\pi$ -conjugated structure. Transparent thin films were deposited electrolytically.

In another aspect this invention applies its conductive polymers in the formation of novel light-emitting diode (LED) structures. References to LEDs and their fabrication include: Burroughs, J.H., Bradley, D.D.C., Brown, A.R., Marks, R.N., Mackay, K., Friend, R.H., Burns, P.L. and Holmes, A.B., Nature, 347, 539-541 (1990); Braun, D. and Heeger, A.J., Applied Physics Letters, 58, 1982-1984 (1991); Burn, P.L., Holmes, A.B., Kraft, A., Bradley, D.D.C., Brown, A.R., Friend, R.H., and Gymer, R.W., Nature, 356, 47-49 (1992); and Grem, G., Leditzky, G., Ulrich, B., and Leising, G., Advanced Materials, 4, 36-38 (1992).

SUMMARY OF THE INVENTION

The present invention relates to electrically conducting polymeric compositions. These compositions include a conductive polyaniline in intimate admixture (solution or the like) with a substrate material. The term "substrate" is used to indicate a range of nonconductive and semiconducting (i.e., conductivity of  $10^{-8}$  S-cm<sup>-1</sup> or less) organic liquids and polymers of dielectric constant below about 22. More particularly, these compositions include polyaniline of film and fiber-forming molecular weight, a substrate and functionalized protonic acid dopant in which the counter-ion has been functionalized to be compatible with the substrate. The substrate can be solid polymer. It can be this polymer in melted (molten) form. It can separately or in addition be organic solvent. As used herein, a "functionalized protonic acid" is a protonic acid, generally denoted as  $H^+(M^--R_p)$ , in which the counter-ion anionic species,  $(M^--R_p)$ , contains  $R_p$  which is a functional group or a connection to a polymer backbone which is chosen to be compatible with the substrate which typically includes nonpolar or weakly polar organic liquids, or solid or molten oligomers or polymers. An illustrative example would be the following:



In cases where the functionalized protonic acid is a liquid or has plastic properties, it may replace some or all of the substrate.

Thus, in one aspect this invention provides highly conductive, highly processible, cost-efficient forms of polyaniline-based conductive polymers. These materials are characterized by having a substrate (as

above described), polyaniline and protonic acid dopant which has a counter-ion selected to be compatible with the substrate. These materials can be solids with a solid polymer substrate, or they can be processible liquids or semisolids with a molten polymer and/or a solvent optionally plus dissolved polymer as the substrate.

The solid products of the invention are characterized by being highly conductive at unexpectedly low concentrations of the polyaniline/dopant conductive species. This conductivity shows that the products present the polyaniline as a continuous (i.e., dissolved) phase rather than as a dispersed particulate phase. Microexamination has verified this in that solid polymer-substrated materials have a continuous web of the polyaniline even at low (less than 10%, even less than 1%, or sometimes even less than 0.1%) polyaniline concentrations.

The products of this invention are also characterized by being capable of being formed in transparent forms depending upon the materials employed.

Another aspect of this invention relates to a method of forming a conductive article from the substrated composition of this invention which comprises the steps of:

- a. forming a solution comprising polyaniline, a substrate including an organic liquid solvent optionally a substrate polymer and a functionalized protonic acid compatible with said solvent and said optional polymer; and
- b. removing all or a portion of said solvent from said solution after or concurrent with shaping the solution into the desired article.

Yet another aspect of this invention relates to a method of forming a conductive article from the composition of this invention which compromises the steps of:

- 5           a. forming a solution comprising polyaniline, a liquid substrate of organic liquid monomers and a functionalized protonic acid compatible with said substrate; and
- b. polymerizing the monomers in said solution, after or concurrent with shaping the solution into the  
10       desired article.

Yet another aspect of this invention relates to methods of forming a conductive article which is a composite, or polyblend of conductive polyaniline with  
15       substrate polymers (for example polyethylene, polypropylene, polystyrene, elastomers, poly(ethylenevinylacetate), polyvinylchloride, etc.) from a solution which compromises the steps of:

- 20           a. forming a solution comprising polyaniline, a solvent and a functionalized protonic acid compatible with the solvent and substrate polymers and one or more substrate polymers (for example polyethylene, polypropylene, polystyrene, elastomers, polyamides, poly(ethylenevinylacetate), polyvinylchloride, etc.); and
- 25           b. removing all or a portion of said solvent from said solution, thereby giving rise to the conductive article.

Yet another aspect of this invention relates to methods of forming a solid conductive article which is a  
30       composite, or polyblend of conductive polyaniline with substrate polymers which compromises the steps of:

- a. forming a solution comprising polyaniline, a monomer precursor to said substrate polymer, a  
35       substrate made of organic liquid monomers and a

functionalized protonic acid solute compatible with said substrate and monomer; and

b. polymerizing the monomer to yield a solid, optionally with solvent removal.

5 Yet another aspect of this invention relates to methods of forming a conductive article of conductive polyaniline with substrate by:

a. forming a melt comprising polyaniline, a functionalized protonic acid solute and a molten polymer substrate selected from the group consisting of nonpolar  
10 or weakly polar thermoplastic polymers; and

b. solidifying said melt.

Any of these processes can additionally contain the step of drawing or otherwise distorting the shape of  
15 the article to improve its physical and electrical properties.

Still another aspect of this invention relates to conductive articles and conductive layers, made from polyblends of polyaniline with one or more substrate  
20 polymers, in accordance with this invention.

The compositions and methods of this invention provide conductive articles, made from polyaniline and one or more substrate polymers, of all shapes, as for example, articles fabricated by injection molding or bulk  
25 extrusion, or articles fabricated by use of the methods of solution processing (for example flexible films, tapes, or fibers), on supports or free-standing, all of which are stable. The articles can be optical quality, or transparent.

30 In a particular embodiment the polymers of the invention are formed into conductive layers for use in light-emitting diodes which can be flexible and colored, if desired.

35

In this aspect, a flexible light-emitting diode which is formed using soluble polyaniline (PANI) cast from a solution onto a flexible polymer substrate as the transparent, flexible, hole-injecting electrode and using  
5 a semiconducting (conjugated) polymer cast from solution as the electroluminescent layer. The semiconducting (conjugated) polymer is present either in the conjugated form (and therefore requiring no subsequent heat treatment at elevated temperatures) or as a precursor  
10 polymer (which is subsequently converted to the semiconducting form by heat treatment at elevated temperatures).

These light-emitting diodes can have flexible conducting polyaniline as the transparent injecting  
15 electrode, semiconducting (conjugated) polymers as the active electroluminescent layer and flexible free-standing organic polymer films as substrates. These LEDs can be formed to turn on at bias voltages compatible with digital electronics (i.e., at voltages less than 5  
20 volts).

#### Brief Description of the Drawings

Figures 1A and B are graphs which show the concentration in solution of a conducting  
25 polyaniline-dodecylbenzsulfonic acid (DBSA) protonic acid complex in xylene as a function of the molar ratio of the total amount of DBSA to aniline repeat unit.

Figure 2A shows a graph of the four-probe electrical conductivity of polyblend films prepared from  
30 xylene solutions of polyaniline-DBSA complex and isotactic polypropylene versus the composition of the films.

Figure 2B shows a graph of the four-probe electrical conductivity of polyblend films prepared from  
35

m-cresol solutions of polyaniline-CSA complex and nylon 12 or nylon 4.6 versus the composition of the films. The open and filled symbols refer to nylon 12 and nylon 4.6, respectively.

5                   Figure 3 is a graph of the four-probe electrical conductivity of polyblend films prepared from xylene solutions of polyaniline-DBSA complex and ultra-high molecular weight polyethylene versus the composition of the films. The open symbols are of  
10 undrawn, (isotropic) films; the filled circles are of the films that were stretched on a hot plate at 105°C to a draw ratio of 40.

                  Figure 4 is a graph of the four-probe electrical conductivity as a function of the composition  
15 of polyblends films that were prepared from chloroform solutions of polyaniline-DBSA complex and polystyrene or poly(3-octylthiophene). The open and filled symbols refer to polystyrene and poly(3-octylthiophene), respectively.

20                   Figure 5 is a graph of the four-probe electrical conductivity of polyblend films prepared from a melt of polyaniline-DBSA complex and polyethylene versus the composition of the films. The open and filled symbols refer to compositions in which the molar ratio of  
25 DBSA to aniline repeat unit (PhN) was 0.5 and 1.0, respectively.

                  Figure 6 is a graph of the four-probe electrical conductivity of polyblend films prepared from a melt of polyaniline-DBSA complex and nylon 12 versus  
30 the composition of the films. The molar ratio of DBSA to aniline repeat unit (PhN) was 0.5.

                  Figure 7 shows a graph of the four-probe electrical conductivity of polyblend films prepared from a melt of polyaniline-DBSA complex and  
35



poly(vinylchlorid ) versus the composition of the films in the absence and presence of the plasticizer Mesamoll. The open triangles and circles refer to compositions in which the molar ratio of DBSA to aniline repeat unit (PhN) was 0.5 and 1.0, respectively. The filled circles refer to compositions in which the molar ratio between PhN, DBSA and Mesamoll was 1:0.5:0.5.

Figure 8 shows a graph of the four-probe electrical conductivity of polyblend films prepared from a melt of polyaniline-dioctylhydrogenphosphate (DOHP) complex and polyvinylchloride versus the composition of the films. The molar ratio of DOHP to aniline repeat unit (PhN) was 0.33.

Figure 9 is a series of visible transmittance spectrographs for three PANi/CSA films;

Figure 10 is a graph of conductivity of PANi/CSA/PMMA films at various PANi concentrations;

Figure 11 is a series of visible transmittance spectrographs for PANi/CSA/PMMA films;

Figure 12 is a series of visible transmittance spectrographs for different thickness PANi/CSA/PMMA films;

Figure 13 is a series of visible transmittance spectrographs for PANi/CSA/PMMA films;

Figure 14 is a series of visible transmittance spectrographs for PANi/CSA/PMMA films;

Figure 15 is a graph of conductivity of PANi/DBSA/PMMA films at various PANi concentrations;

Figure 16 is a graph of conductivity of PANi/CSA/PVAc films at various PANi concentrations;

Figure 17 is a series of visible transmittance spectrographs for PANi/CSA/PVAc films;

Figure 18 is a graph of conductivity of PANi/CSA/PC films at various PANi concentrations;

Figure 19 is a graph of conductivity of PANi/CSA/poly(acrylonitrile) films at various PANi concentrations; and

Figure 20 is a series of visible transmittance spectrographs for various PANi/CSA/polymer films.

Figure 21 is a semi-schematic perspective view of an LED of this invention.

Figure 22 is a graph of absorbance and photoluminescence as a function of wavelength for an LED of this invention.

Figure 23 is a graph of current as a function of bias voltage for an LED of this invention.

Figure 24 is a graph of light intensity observed with these LEDs as a function of bias voltage.

#### DETAILED DESCRIPTION OF THE INVENTION

The conductive materials and layers provided and employed in this invention typically include three types of ingredients.

(i) One or more substituted or unsubstituted polyanilines;

(ii) An organic substrate phase. This can be a solid or fluid phase. It can be an organic liquid. It can also be an organic solid or semisolid such as melted or softened polymer, or in a special circumstance can be the protonic acid (iii) when it is a liquid and not overly polar in overall character--i.e., when it has a large nonpolar region. It can be mixtures of two or more of these materials. It has a dielectric constant below about 22.

(iii) One or more functionalized protonic acid solutes in which the counter-ion has been functionalized to be compatible with the substrate.

By proper selection, these materials can provide transparent conductive products.

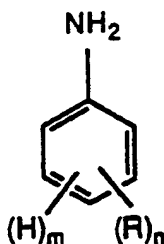
The Polyaniline

5 One ingredient is substituted or unsubstituted polyaniline. When the term "polyaniline" is used in this application, it is used generically to include substituted and unsubstituted materials, unless the context is clear that only the specific nonsubstituted  
10 form is intended. In general, polyanilines for use in the invention are polymers and copolymers of film and fiber-forming molecular weight derived from the polymerization of unsubstituted and substituted anilines of the Formula I:

15

Formula I

20



wherein

n is an integer from 0 to 4;

m is an integer from 1 to 5 with the proviso

25 that the sum of n and m is equal to 5; and

R is independently selected so as to be the same or different at each occurrence and is selected from the group consisting of alkyl, alkenyl, alkoxy, cycloalkyl, cycloalkenyl, alkanoyl, alkythio, aryloxy, alkylthioalkyl, alkylaryl, arylalkyl, amino, alkylamino, dialkylamino, aryl, alkylsulfinyl, alkoxyalkyl, alkylsulfonyl, arylthio, arylsulfinyl, alkoxycarbonyl, arylsulfonyl, carboxylic acid, halogen, cyano, or alkyl  
35 substituted with one or more sulfonic acid, carboxylic

acid, halo, nitro, cyano or expoly moieties; or  
carboxylic acid, halogen, nitro, cyano, or sulfonic acid  
moieties; or any two R groups together may form an  
alkylene or alkenylene chain completing a 3, 4, 5, 6 or  
5 7-membered aromatic or alicyclic ring, which ring may  
optionally include one or more divalent nitrogen, sulfur  
or oxygen atoms. Without intending to limit the scope of  
this invention, the size of the various R groups ranges  
from about 1 carbon (in the case of alkyl) through 2 or  
10 more carbons up through about 20 carbons with the total  
of n Rs being from about 1 to about 40 carbons.

Illustrative of the polyanilines useful in the  
practice of this invention are those of the Formula II to  
V:

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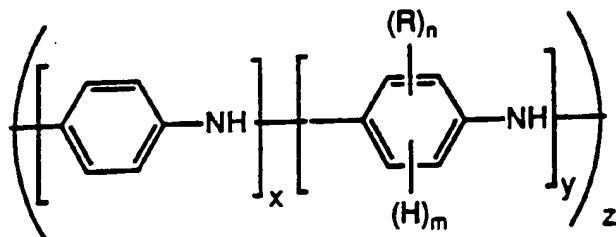
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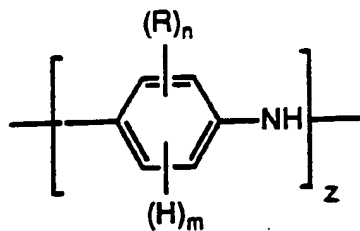
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II

10 or

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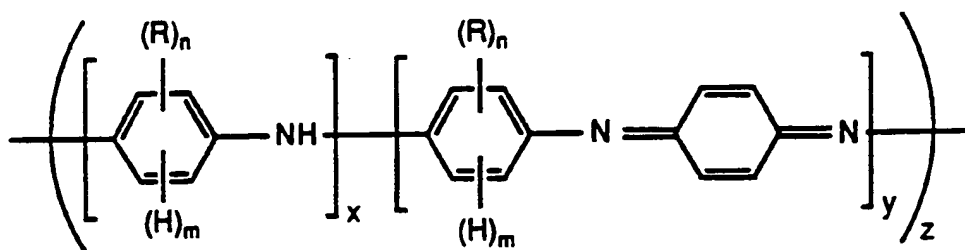


III

or

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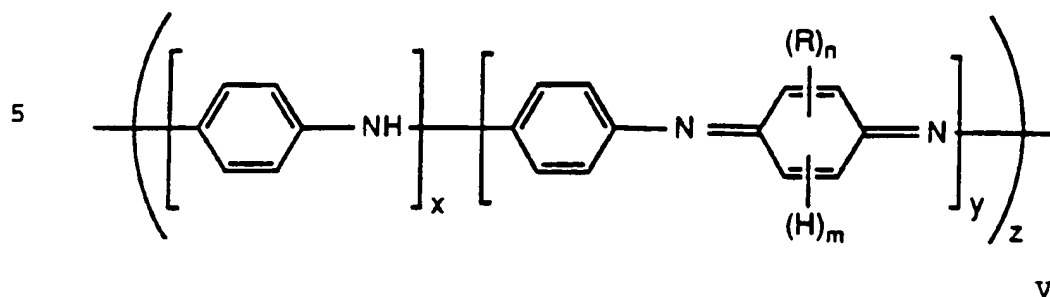


IV

30

35

or



15

wherein:

n, m and R are as described above except that m is reduced by 1 as a hydrogen is replaced with a covalent bond in the polymerization and the sum of n plus m equals 4;

y is an integer equal to or greater than 0;

x is an integer equal to or greater than 1,

with the proviso that the sum of x and y is greater than 1; and

20 z is an integer equal to or greater than 1.

The following listing of substituted and unsubstituted anilines are illustrative of those which can be used to prepare polymers and copolymers useful in the practice of this invention.

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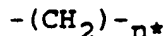
Aniline	2,5-Dimethylaniline
o-Toluidine	2,3-Dimethylaniline
m-Toluidine	2,5-Dibutylaniline
o-Ethylaniline	2,5-Dimethoxyaniline
30 m-Ethylaniline	Tetrahydronaphthylamine
o-Ethoxyaniline	o-Cyanoaniline
m-Butylaniline	2-Thiomethylaniline
m-Hexylaniline	2,5-Dichloroaniline
35 m-Octylaniline	3-(n-Butanesulfonic acid)

	4-Bromoaniline	aniline
	2-Bromoaniline	
	3-Bromoaniline	2,4-Dimethoxyaniline
	3-Acetamidoaniline	4-Mercaptoaniline
5	4-Acetamidoaniline	4-Methylthioaniline
	5-Chloro-2-methoxyaniline	3-Phenoxyaniline
	5-Chloro-2-ethoxyaniline	4-Phenoxyaniline

10 Illustrative of useful R groups are alkyl, such  
 as methyl, ethyl, octyl, nonyl, tert-butyl, neopentyl,  
 isopropyl, sec-butyl, dodecyl and the like, alkenyl such  
 as 1-propenyl, 1-butenyl, 1-pentenyl, 1-hexenyl,  
 1-heptenyl, 1-octenyl and the like; alkoxy such as  
 15 propoxy, butoxy, methoxy, isopropoxy, pentoxy, nonoxy,  
 ethoxy, octoxy, and the like, cycloalkenyl such as  
 cyclohexenyl, cyclopentenyl and the like; alkanoyl such  
 as butanoyl, pentanoyl, octanoyl, ethanoyl, propanoyl and  
 the like; alkylsulfinyl, alkylsulfonyl, alkylthio,  
 20 arylsulfinyl, arylsulfonyl, and the like, such as  
 butylthio, neopentylthio, methylsulfinyl, benzylsulfinyl,  
 phenylsulfinyl, propylthio, octylthio, nonylsulfonyl,  
 octylsulfonyl, methylthio, isopropylthio, phenylsulfonyl,  
 methylsulfonyl, nonylthio, phenylthio, ethylthio,  
 25 benzylthio, phenethylthio, naphthylthio and the like;  
 alkoxycarbonyl such as methoxycarbonyl, ethoxycarbonyl,  
 butoxycarbonyl and the like, cycloalkyl such as  
 cyclohexyl, cyclopentyl, cyclooctyl, cycloheptyl and the  
 like; alkoxyalkyl such as methoxymethyl, ethoxymethyl,  
 30 butoxymethyl, propoxyethyl, pentoxybutyl and the like;  
 aryloxyalkyl and aryloxyaryl such as phenoxyphenyl,  
 phenoxyethylene and the like; and various substituted  
 alkyl and aryl groups such as 1-hydroxybutyl,  
 1-aminobutyl, 1-hydroxylpropyl, 1-hydroxypentyl,  
 35

1-hydroxyoctyl, 1-hydroxyethyl, 2-nitroethyl, trifluoromethyl, 3,4-epoxybutyl, cyanomethyl, 3-chloropropyl, 4-nitrophenyl, 3-cyanophenyl, and the like; sulfonic acid terminated alkyl and aryl groups and  
5 carboxylic acid terminated alkyl and aryl groups such as ethylsulfonic acid, propylsulfonic acid, butylsulfonic acid, phenylsulfonic acid, and the corresponding carboxylic acids.

Also illustrative of useful R groups are  
10 divalent moieties formed from any two R groups such as moieties of the formula:



15 wherein  $n^*$  is an integer from about 3 to about 7, as for example  $-(CH_2)_4$ ,  $-(CH_2)_3$  and  $-(CH_2)_5$ , or such moieties which optionally include heteroatoms of oxygen and sulfur such as  $-CH_2SCH_2-$  and  $-CH_2OCH_2-$ . Exemplary of other  
20 useful R groups are divalent alkenylene chains including 1 to about 3 conjugated double bond unsaturation such as divalent 1,3-butadiene and like moieties.

Preferred for use in the practice of this invention are polyanilines of the above Formulas II to V in which:

25  $n$  is an integer from 0 to about 2;  
 $m$  is an integer from 2 to 4, with the proviso that the sum of  $n$  and  $m$  is equal to 4;  
 $R$  is alkyl or alkoxy having from 1 to about 12 carbon atoms, cyano, halogen, or alkyl substituted with  
30 carboxylic acid or sulfonic acid substituents;  
 $x$  is an integer equal to or greater than 1;  
 $y$  is an integer equal to or greater than 0,  
with the proviso that the sum of  $x$  and  $y$  is greater than about 4, and

35



z is an integer equal to or greater than about

5.

Particularly preferred for use in the practice of this invention are polyanilines of the above Formulas II to V in which:

n is an integer from 0 to 2;

m is an integer from 2 to 4, with the proviso that the sum of n and m is equal to 4;

R is alkyl or alkoxy having from 1 to about 4 carbon atoms or alkyl substituted with carboxylic acid or sulfonic acid substituents;

x is an integer equal to or greater than 1;

y is an integer equal to or greater than 0,

with the proviso that the sum of x and y is greater than about 6; and

z is an integer equal to or greater than about

10.

Amongst the particularly preferred embodiments, most preferred for use in the practice of this invention are polyanilines of the above Formulas II to V in which:

n is an integer, 0 or 1;

m is an integer, 3 or 4, with the proviso that the sum of n and m is equal to 4;

R is alkyl or alkoxyl from 1 to about 4 carbon atoms;

x is an integer equal to or greater than 2;

y is an integer equal to or greater than 1,

with the proviso that the sum of x and y is greater than about 8; and

z is an integer equal to or greater than about

15.

In the most preferred embodiments of this invention, the polyaniline is derived from unsubstituted

aniline, i.e., where n is 0 and m is 5 (monomer) or 4 (polymer).

In general, the polyanilines particularly useful in the practice of this invention are those which are of "film and fiber-forming molecular weight." As used herein, "film and fiber-forming molecular weight" generally means weight average molecular weights which exceed about 10,000 daltons. Solutions of such soluble polymers generally can be cast to form thin, freestanding films or extruded into films and fibers which are coherent and retain their shape, and preferably are not brittle when bent.

In general, an advantage of this invention is that substituted and unsubstituted polyanilines in the protonated conducting form may be dissolved in organic liquids and such polyanilines have more than 8 monomer repeat units. These are more highly condensed than the polyanilines described in United States Patent Nos. 3,963,498 and 4,025,463. Because of the higher molecular weight, the present substituted and unsubstituted polyanilines can be coated onto surfaces and spun into fibers without the need for binders, i.e., polymer compositions which bind and improve the stability of the polyanilines which is not generally true of the low molecular weight oligomeric polyanilines described in United States Patent Nos. 3,963,498 and 4,025,463. The molecular weight of the substituted or unsubstituted polyaniline at which the polymer will be film or fiber-forming may vary widely, depending on a number of factors including the number of repeat units, and the number of substituents and the substituent pattern. In general, substituted and unsubstituted polyanilines will be of film and fiber-forming molecular weight where the number of monomer repeat units is at least about 50. In the

preferred embodiments of the invention, the number of repeat units is at least about 75, and in the particularly preferred embodiments, the number of repeat units is at least about 200. Amongst the particularly preferred embodiments, most preferred are those  
5       embodiments in which the number of repeat units is at least about 250.

The polyaniline can be conveniently used in the practice of this invention in any of its physical forms.  
10       Illustrative of useful forms are those described in Green, A.G., and Woodhead, A. E., "Aniline-black and Allied Compounds, Part 1," J. Chem. Soc., Vol. 101, pp. 1117 (1912) and Kobayashi, et al., "Electrochemical Reactions . . . of Polyaniline Film-Coated Electrodes,"  
15       J. Electroanal. Chem., Vol. 177, pp. 281-91 (1984), which are hereby incorporated by reference. For unsubstituted polyaniline, useful forms include leucoemeraldine, protoemeraldine, emeraldine, nigraniline and tolu-  
20       protoemeraldine forms.

Useful polyanilines can be prepared through use of chemical synthetic procedures. For example, one form of polyaniline having at least about 160 repeat units can be prepared by treating aniline with ammonium persulfate ( $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ) in excess 1M HCl. This powdered form of  
25       polyaniline is blue green in color. After methanol washing and air drying this material exhibits a conductivity of about  $10 \text{ S-cm}^{-1}$ . This conductive form of polyaniline can be treated with ammonium hydroxide in ethanol to form a nonconductive form of polyaniline which  
30       is purple in color and which has a conductivity of less than  $10^{-8} \text{ S-cm}^{-1}$ . Other chemical procedures for preparation of various chemical forms of polyaniline are described in detail in Green et al. described above.

Useful forms of polyaniline can also be prepared electrochemically. For example, useful forms of polyaniline can be prepared by the electrochemical oxidation of aniline in aqueous fluoroboric acid electrolyte on a platinum foil anode.

#### The Functionalized Protonic Acid

A second ingredient of the conductive composition of this invention is a "functionalized protonic acid" in which the counter-ion has been functionalized to be compatible with nonconductive liquid or polymer substrates. As used herein, a "protonic acid" is an acid that protonates the polyaniline to form a complex with said polyaniline, which complex has a conductivity equal to or greater than about  $10^{-11}$  S/cm. Preferred protonic acids are those that protonate the polyaniline to form a complex, said complex having an electrical conductivity of greater than about  $10^{-6}$  S/cm, and particularly preferred protonic acids are those that form a complex with the polyaniline having a conductivity of greater than about  $10^{-3}$  S/cm. Amongst these particularly preferred embodiments, most preferred are those protonic acids which form a polyaniline complex having a conductivity of greater than 0.1 S/cm. Protonic acids are well known as dopants in the conductive polymer art as shown by the reference to J.C. Chiang and Alan G. MacDiarmid; and the reference to W.R. Salaneck et al., noted above, but are not necessarily compatible with nonconductive substrates such as nonpolar or weakly polar organic liquids. As used herein a "functionalized" protonic acid is an acid that protonates the polyaniline to form a complex with said polyaniline, which complex has a conductivity equal to or greater than about  $10^{-1}$  S/cm<sup>-1</sup> and which has been functionalized to be miscible

35

with or soluble in (as opposed to merely dispersible in) the substrate which makes up the third component of these products. In view of these properties, the acid can be considered a solute and the substrate a solvent.

5           This functionalization allows the polyaniline complex to be homogenized into the substrate through solubilization, or the like. This dissolving and/or intimate mixing leads to an essentially continuous network of the conductive species in the substrate. The  
10       substrate can be present as a discontinuous phase or preferably as a co-continuous phase. This imparts a high level of conductivity to the overall composition--a conductivity many times higher than would be achieved if the conductive species were present as suspended  
15       particles or the like.

          As will be set out below, the substrate phases which are employed include organic liquids and/or melted polymers. In determining "compatibility" between a  
20       functionalized protonic acid and a substrate, the usual chemical solubility-miscibility rules are followed. For example with more polar substrates such as ketones or esters (as organic solvents) or poly(esters),  
poly(arylates) or poly(amides) as polymers--  
functionalization in the protonic acid counter-ion should  
25       promote or at minimum not substantially diminish the polar nature of the counter-ion group.

          Conversely, with the preferred nonpolar or weakly polar substrates such as, for example, alkanes or aromatic hydrocarbons or halohydrocarbons as liquids or  
30       poly(olefins), vinyl polymers, such as polystyrene, polymethacrylates, or elastomers, such as ethylene propylene diene monomer copolymers as polymer substrates--  
functionalization should impart a nonpolar or weakly polar region to the counter-ion (for example adding a  
35

hydrocarbon tail to the counter-ion) so as to enhance or impart solubility of the counter-ion into the nonpolar substrate.

In one sense, in the case of nonpolar substrates, the acid is acting as a surfactant and thereby renders the polar counter-ion compatible with nonpolar or weakly polar organic substrates. In general, functionalized protonic acids for use in the invention are those of Formulas VI and VII:

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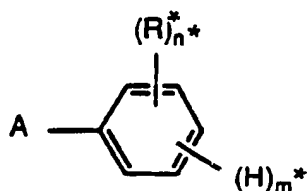


VI

or

15

20



VII

wherein:

A is sulfonic acid, selenic acid, phosphonic acid, boric acid or a carboxylic acid group; or hydrogen sulfate, hydrogen selenate, hydrogen phosphate;

$n^*$  is an integer from 0 to 5;

$m^*$  is an integer from 0 to 4 with the proviso that the sum of  $n$  and  $m$  is 5;

$R_1$  is alkyl, alkenyl, alkoxy, alkanoyl, alkylthio, alkylthioalkyl, having from 1 to about 20 carbon atoms; or alkylaryl, arylalkyl, alkylsulfinyl, alkoxyalkyl, alkylsulfonyl, alkoxycarbonyl, carboxylic acid, where the alkyl or alkoxy has from 0 to about 20

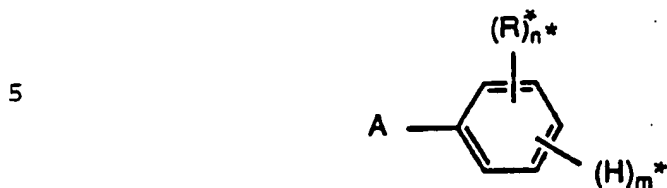
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carbon atoms; or alkyl having from 3 to about 20 carbon atoms substituted with one or more sulfonic acid, carboxylic acid, halogen, nitro, cyano, diazo, or epoxy moieties; or a substituted or unsubstituted 3, 4, 5, 6  
5 or 7 membered aromatic or alicyclic carbon ring, which ring may include one or more divalent heteroatoms of nitrogen, sulfur, sulfinyl, sulfonyl or oxygen such as thiophenyl, pyrolyl, furanyl, pyridinyl.

In addition to these monomeric acid forms,  $R_1$   
10 can be a polymeric backbone from which depend a plurality of acid functions "A." Examples of polymeric acids include sulfonated polystyrene, sulfonated polyethylene and the like. In these cases the polymer backbone can be selected either to enhance solubility in nonpolar  
15 substrates or be soluble in more highly polar substrates in which materials such as polymers, polyacrylic acid or poly(vinylsulfonate), or the like, can be used.

$R^*$  is the same or different at each occurrence and is alkyl, alkenyl, alkoxy, cycloalkyl, cycloalkenyl,  
20 alkanoyl, alkylthio, aryloxy, alkylthioalkyl, alkylaryl, arylalkyl, alkylsulfinyl, alkoxyalkyl, alkylsulfonyl, aryl, arylthio, arylsulfinyl, alkoxycarbonyl, arylsulfonyl, carboxylic acid, halogen, cyano, or alkyl substituted with one or more sulfonic acid, carboxylic  
25 acid, halogen, nitro, cyano, diazo or epoxy moieties; or any two R substituents taken together are an alkylene or alkenylene group completing a 3, 4, 5, 6 or 7 membered aromatic or alicyclic carbon ring or multiples thereof, which ring or rings may include one or more divalent  
30 heteroatoms of nitrogen, sulfur, sulfinyl, sulfonyl or oxygen.  $R^*$  typically has from about 1 to about 20 carbons especially 3 to 20 and more especially from about 8 to 20 carbons. It will be appreciated that the

depiction of the acids as  $A-R_1$  is equivalent to their earlier depiction as  $H^+(M^-R_p)$  and that the



acids fall within the general structure of  $A-R_1$ .

10 Preferred for use in the practice of this invention are functionalized protonic acid solutes of the above Formulas VI and VII in which:

A is sulfonic acid, phosphonic acid or carboxylic acid;

15  $n^*$  is an integer from 1 to 5;

$m^*$  is an integer from 0 to 4 with the proviso that the sum of n and m is 5;

$R_1$  is alkyl, alkenyl, alkoxy, alkanoyl, alkylthio, alkylthioalkyl, having from 5 to about 16 carbon atoms; or alkylaryl, arylalkyl, alkylsulfinyl, 20 alkoxyalkyl, alkylsulfonyl, alkoxycarbonyl, carboxylic acid, where the alkyl or alkoxy has from 1 to about 20 carbon atoms; or alkyl having from 3 to about 20 carbon atoms substituted with one or more sulfonic acid, 25 carboxylic acid, halogen, nitro, cyano, diazo, or epoxy moieties;

$R^*$  is the same or different at each occurrence and is alkyl, alkenyl, alkoxy, arylalkyl, alkylsulfonyl, alkoxycarbonyl or carboxylic acid having from 3 to 12 30 carbon atoms, or alkyl substituted with one or more carboxylic acid, halogen, diazo or epoxy moieties;

Particularly preferred for use in the practice of this invention are functionalized protonic acid solutes of the above Formulas VI and VII in which:

35



A is sulfonic acid or carboxylic acid;

$n^*$  is an integer from 1 to 3;

$m^*$  is an integer from 0 to 4 with the proviso  
that the sum of  $n$  and  $m$  is 5;

5  $R_1$  is alkyl, alkenyl, alkoxy, having from 6 to  
about 14 carbon atoms; or arylalkyl, where the alkyl or  
alkyl portion or alkoxy has from 4 to about 14 carbon  
atoms; or alkyl having from 6 to about 14 carbon atoms  
substituted with one or more, carboxylic acid, halogen,  
10 diazo, or epoxy moieties;

$R^*$  is the same or different at each occurrence  
and is alkyl, alkoxy, alkylsulfonyl, having from 4 to 14  
carbon atoms, or alkyl substituted with one or more  
halogen moieties again with from 4 to 14 carbons in the  
15 alkyl.

Among the particularly preferred embodiments,  
most preferred for use in the practice of this invention  
are functionalized protonic acid solutes of the above  
Formulas VI and VII in which:

20 A is sulfonic acid;

$n^*$  is the integer 1 or 2;

$m^*$  is the integer 3 or 4 with the proviso that  
the sum of  $n$  and  $m$  is 5;

$R_1$  is alkyl or alkoxy, having from 6 to about  
25 14 carbon atoms; or alkyl having from 6 to about 14  
carbon atoms substituted with one or more halogen  
moieties;

$R^*$  is alkyl or alkoxy, having from 4 to 14,  
especially 12 carbon atoms, or alkyl substituted with one  
30 or more halogen, moieties.

In the most preferred embodiments of this  
invention, the functionalized protonic acid solute is  
dodecylbenzene sulfonic acid.

The amount of functionalized protonic acid employed can vary depending on the degree of conductivity required. In general, sufficient functionalized protonic acid is added to the polyaniline-containing admixture to

5 form a conducting material. Usually the amount of functionalized protonic acid employed is at least sufficient to give a conductive polymer (either in solution or in solid form) having a conductivity of at least about  $10^{-9}$  S-cm<sup>-1</sup>. As a general rule, the amount

10 needed will be much lower, i.e., 10% by weight (basis overall composition) or less than would be expected to impart the desired conductivity. This is because the functionalized counter-ion of the protonic acid is dissolved or intimately mixed in the substrate rather

15 than merely dispersed or suspended in it. The upper level of conductivity is not critical and may depend on the type of aniline polymer employed. In general, the highest level of conductivity obtained is provided without unduly adversely affecting the environmental

20 stability of the polymer. In the preferred embodiments of the invention the amount of functionalized protonic acid employed is sufficient to provide a conductivity of at least about  $10^{-10}$  S-cm<sup>-1</sup>, and in the particularly preferred embodiments is sufficient to provide a

25 conductivity of at least about  $10^{-8}$  S-cm<sup>-1</sup>. Amongst these particularly preferred embodiments, most preferred are those embodiments in which unsubstituted polyaniline is employed and in which sufficient acid is employed to provide a conductivity of at least about  $10^{-6}$  S-cm<sup>-1</sup>.

30 The Substrate

An optional third component of the materials of this invention is a substrate. Substrates are insulating or semiconducting materials. The substrate can be an

35 organic solvent, or it can be bulk oligomeric or

polymeric or prepolymeric materials which can be put into a fluid (liquid or semisolid) form during processing so as to achieve the required intimate mixture (solution or the like) with the polyaniline and dopant. In the case of nonpolar counter-ions, it is preferred to use nonpolar or weakly polar solvents or polymers as substrates. As used herein the terms "nonpolar or weakly polar organic solvent, or oligomeric or polymer liquid" and the like refer to a material which is or can be rendered fluid by melting and which has a dielectric constant at room temperature equal to or less than about 22. Preferred of these substrates are those common organic solvents, or meltable malleable oligomers or polymers with dielectric constants equal to or less than about 15. Especially preferred nonpolar substrates are those solvents, or oligomers or polymers with dielectric constants equal to or less than about 10.

Illustrative of useful common solvents are the following materials: substituted or unsubstituted aromatic hydrocarbons such as benzene, toluene, p-xylene, m-xylene, naphthalene, ethylbenzene, styrene, aniline and the like; higher alkanes such as pentane, hexane, heptane, octane, nonane, decane and the like; cyclic alkanes such as decahydronaphthalene; halogenated alkanes such as chloroform, bromoform, dichloromethane and the like; halogenated aromatic hydrocarbons such as chlorobenzene, o-dichlorobenzene, m-dichlorobenzene, p-dichlorobenzene and the like; alcohols such as m-cresol, benzylalcohol, 2-butanol, 1-butanol, hexanol, pentanol, decanol, 2-methyl-1-propanol and the like; higher ketones such as hexanone, butanone, pentanone and the like; heterocyclics such as morpholine; perfluorinated hydrocarbons such as perfluorodecaline, perfluorobenzene and the like. Mixtures of such nonpolar

organic solvents can also be used as for example mixtures of xylene and chlorobenzene.

Examples of semiconducting (i.e., materials with conductivities of up to  $10^{-8}$  S-cm<sup>-1</sup>) include undoped  
5 or lightly doped conjugated homo- or copolymers such as polythiophenes, polypyrroles, polyacetylenes, poly-paraphenylene sulfide, poly(paraphenylene vinylenes), and the like.

Other useful substrates include liquefiable  
10 (melttable) bulk oligomers or polymers. Illustrative of useful oligomeric liquids are liquefiable higher alkanes such as hexatriacontane, dotriadecane, octadodecane; branched higher alkanes and waxes, and perfluorinated higher alkanes and waxes. Illustrative of useful  
15 polymeric substrates are liquefiable polyethylenes, isotactic polypropylene, polystyrene, poly(vinylalcohol), poly(ethylvinylacetate), polybutadienes, polyisoprenes, ethylenevinylene-copolymers, ethylene-propylene copolymers, poly(ethyleneterephthalate),  
20 poly(butyleneterephthalate) and nylons such as nylon 12, nylon 8, nylon 6, nylon 6.6 and the like. Mixtures of organic solvents plus polymers may be used in which case the solvent can serve as a plasticizer for the polymer.

Organic substrates selected for use in any  
25 particular situation will depend primarily on the various R substituents of the polyaniline, and/or of the functionalized protonic acid, and/or one or more other polymers that are selected to form a blend with the substituted or unsubstituted polyaniline. In general,  
30 less polar substituents and/or less polar other polymers used the preparation of polyblends, will require lower dielectric constants. Conversely, more polar substituents and/or more polar other polymers used the

preparation of composites or polyblends, will require higher dielectric constants.

Preferred common organic solvents are toluene, xylenes, styrene, aniline, decahydronaphthalene, chloroform, dichloromethane, chlorobenzenes, morpholine, and particularly preferred solvents are toluene, xylenes, decahydronaphthalene, and chloroform. Amongst these embodiments are those in which the solvents are aromatic hydrocarbons such as xylene, and halogenated hydrocarbons such as chloroform.

#### Overall Proportions

The proportions of materials are not critical and can vary widely. However, the following guidelines are believed important for achieving materials particularly useful in the present invention. The amount of functionalized protonic acid may play a part in determining whether a plasticized composition or a solution is formed. In general, the higher the degree of protonation (with associated functionalized counter-ions), the greater the solvency of the protonated conducting polymer in the solvent. Conversely, the lower the degree of protonation (and the lower the concentration of functionalized counter-ions), the less the solvency of the conducting polymer in the solvent, but the polymer is still plasticizable. For example, as shown in Examples 5 and 6, in the case of unsubstituted polyaniline where the level of protonation is about 1.0 or more equivalents of functionalized protonic acid per aniline repeat unit, soluble conductive polyaniline is provided. However, where the level of protonation is less than about one equivalent of protonic acid per aniline repeat unit, plasticizable conductive polymers are formed. As noted above, sufficient protonation occurs to form either the soluble conductive polymer or

plasticized conductive polymer. In a preferred embodiment of this invention, the level of protonic acid addition is such that solutions of conductive polymers are obtained.

5           In general, the amount of solvent substrate as a proportion of the amount of solution is not believed to be critical, since any amount as a liquid or semisolid will form at least a viscous gel with the protonated conductive polymers. These viscous embodiments of the  
10 invention are particularly useful for silkscreening conductive circuitry and for applying thick film coating on substrates. For other applications, it may be preferred, however, to use sufficient liquid solvent to lower the viscosity of the gel or solution to a point  
15 where it flows at least sufficiently to conform to a container shape or mold in a reasonably short period of time, e.g., in 30 minutes or less; or the be extruded into films and fibers. Preferably, the liquid is present in sufficient amounts to lower the viscosity of the  
20 solution to less than about 10,000 centipoise, and more preferably from about 1 to about 1000 centipoise.

As just described, the conductive polymer compositions of this invention include polyaniline, protonic acid, and solvent or plasticizer substrate  
25 (which can be protonic acid in some cases, as already noted). The relative proportions of these materials can range as follows:

0.01% to 100% by weight of polyaniline plus  
protonic acid  
30           99.99% to 0% of substrate, preferably  
0.01% to 99% by weight of polyaniline plus  
protonic acid,  
99.99% to 1% of substrate, and more preferably

0.05 to 50% of polyaniline plus protonic acid  
and

99.95 to 50% of substrate.

These proportions can be expressed for very  
5 preferred compositions to include

Polyaniline	1 part by weight.
Protonic acid	From at least 1 protonic acid
10	proton for each 10 repeat units
	of aniline and preferably at
	least one for each 8 repeat
	units up to 20 protonic acid
	protons for each aniline repeat
15	unit--typically from 0.01 parts
	to 20 parts by weight.
Substrate	0.1 parts to 500 parts,
(including excess	especially 0.2 to 200 parts.
acid)	

20

In addition to the polyaniline homopolymer or  
copolymer, functionalized protonic acid and substrate the  
compositions of this invention can include other optional  
ingredients. The nature of such optional ingredients can  
25 vary widely, and include those materials which are known  
to those of skill in the art for inclusion in polymer  
articles. In the case of dissolvable components,  
materials may be present which alter the physical or  
mechanical properties of either the solution or the  
30 articles eventually derived from the solution. Examples  
of such materials include plasticizers, oligomers or  
other conventional polymers such as polycarbonate,  
polyacrylonitrile, polyvinyl chloride, polyvinylidene  
chloride, polyvinyl alcohol, polyethylene oxide,

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polystyrene, nylon, cellulose acetate butyrate, polypropylene, polyethylene, polypropylene cellulose acetate, polyphenylene oxides and the like. In the case of non-soluble fourth components, materials may be present which either fill or form a base for the conductive polymer cast from the composition. These fourth components may include other conductive polymers, other polymers such as poly(3-alkylthiophenes) which may become conductive upon doping, graphite, metal conductors, reinforcing fibers and inert fillers (such as clays and glass). These fourth components can be present in as much as 98% of the total mixture, and being optional can be omitted altogether. Usually, for commercially attractive products these added fourth components make up 2% to 95% by weight of the total final product.

#### Processing

The method of forming the compositions of this invention can vary widely. It is important, however, that at some stage the substrate be processed with the polyaniline and dopant in a fluid (liquid, semisolid, or molten form) to assure proper intimate admixture.

For example, one method of forming the present products containing the protonated aniline polymer and the functionalized counter-ions is to react, simultaneously, the aniline polymer, the functionalized protonic acid and solvent as a liquid. Thus, for example, by introducing polyaniline as a solid powder, xylene as a liquid and dodecylbenzene sulfonic acid (DBSA) as a liquid into a mixing vessel, a solution of the protonated conductive polymer is formed, from which conductive polymer can be cast. The conditions of such mixing are not critical, provided that sufficient DBSA is used to dope the desired quantity of polymer and



sufficient solvent is employed to reduce the viscosity of the solution to manageable levels.

An alternate technique of preparing the product of this invention containing the protonated conductive polymer is to mix first the polymer and the solvent, thereafter add the functionalized protonic acid to the solution or two phase system. Thus, for example, if polyaniline powder is admixed with xylene solvent, the powder will remain suspended in the solvent for extended periods under normal conditions. The addition of a functionalized protonic acid to this suspension, such as DBSA, causes the powder to be protonated and, thereafter, causes the protonated conductive polymer to swell and go into solution.

In another method, the solid polymer powder is first mixed with the functionalized protonic acid, such as DBSA, which causes the polymer to be protonated. Subsequently, the protonated polymer is admixed with, for example, xylene and a solution is formed.

Another method for the preparation of solutions containing the polyaniline homopolymer or copolymer and the functionalized protonic acid is where the polymer is synthesized directly in the presence of the functionalized protonic acid and in the non-polar or weakly polar solvent or plasticizing liquid, as described in Example 16. This method is of special interest because the functionalized protonic acid acts as a surfactant in this emulsion polymerization, and yields high molecular weights of the polymers, and high conductivities of the resulting materials derived from the emulsions.

In another method, materials of the present invention can be prepared in three steps. First a soluble conducting polyaniline complex consisting of

polyaniline in the emeraldine salt form complexed with  $(M^- - R_p)$  as counter-ion where  $H^+(M^- - R_p)$  is a functionalized protonic acid. An illustrative example would be



Then the soluble conducting polyaniline complex is co-dissolved with a desired amount of PMMA or any other suitable amorphous bulk polymer in a suitable organic solvent. The concentrations of the two components (the conducting polyaniline complex and, for example, the PMMA) are chosen so as to give a desired ratio in the final conducting film (which may be transparent after casting onto the base and evaporation of the solvent).

The conducting film is then cast onto a base for use as an electrode, an anti-static coating, etc. The detailed method of casting (spin-casting drop-casting, use of a doctor blade, etc.) is chosen to be consistent with secondary criteria (for example, ease of manufacture, cost, shape of substrate, etc).

An alternative route has two steps. First, a polyblend of conducting substituted or unsubstituted polyaniline complex and PMMA (or another amorphous, melt-processible bulk polymer) is prepared using the methods just described followed by evaporation of the solvent to yield a solid polyblend of the desired composition. A film is formed by melting and coating the conducting polyblend onto a desired surface. This alternative has the specific advantage that conducting electrodes can be formed directly onto a base with a complex surface.

After forming the products or forms, including the conductive polymers of this invention, one can often

enhance their physical or electrical properties by drawing or otherwise distorting them. This process and guidelines to its successful use are set out in the Examples.

5           Various methods are contemplated for using the solution or plasticized composition of the present invention. The solvent can be removed from the solution through use of any conventional solvent removal method but is removed preferably by evaporation. Alternatively,  
10   the solvent and unreacted functionalized protonic acid can be removed by extraction with an extractant in which the solvent and unreacted functionalized protonic acid are substantially more soluble than the doped polymer. If liquefied or molten oligomers or polymers are used as  
15   the substrate, solid conducting articles can be formed simply by cooling the liquid composition, as is commonly performed in injection molding, melt extrusion, etc. Alternatively, when polymerizable monomers are employed as the solvent, solid conducting articles can be formed  
20   by polymerizing the monomer. In the two latter methods removal of the solvent is not required.

As will be appreciated by those skilled in polymer processing, the ability to form shaped polymer articles by removing a solvent from a solution enables  
25   one to prepare articles of a wide variety of shapes and sizes. Thus, for example, by removing volatiles from the present solution or plasticized composition spread on a surface, films of any desired thickness can be prepared. By extruding the solution through a die, fibers or films  
30   can be made. Similarly, by removing volatiles from the solution or plasticized composition in a mold of various shapes, shaped articles conforming in shape to the mold can be prepared. It will be appreciated that some shrinkage might occur between the solution in its last  
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flowable state to the final article, but such shrinkage is conventionally accounted for in molding polymers from solution. It is also contemplated that, once a solution or melt is formed, a partial or substantial removal of solvent will occur prior to placing the solution or melt on a surface or in a mold, with the final venting of a solvent occurring on the surface or in the mold. It is contemplated that, if fourth or additional soluble components are introduced into the solution, they will, unless also volatile, be present in the shaped article formed. If the fourth component is a non-volatile liquid, then the removal of volatile components may leave a new liquid or plasticized form of protonated conducting polymer or undoped-neutral polymer. If the additional components are volatile, then foamed or expanded cellular forms of the polymer may be formed.

In the event that fourth or additional nonsoluble components are present (or suspended) in the solution or melt, the protonated conductive polymer will form around, or be filled with, the insoluble material. If, for example, the additional components are glass fibers, the relative amounts of fibers and protonated conductive polymer remaining will cause either the polymer to be fiber-filled, the fibers to be polymer coated or impregnated, or some intermediate composite of fibers and protonated conductive polymer to be formed. In the case of systems wherein the amount of non-soluble component greatly exceeds the protonated conductive polymer remaining, individual particles or shapes of non-soluble components coated or impregnated with protonated conductive polymer will be formed. Examples of articles formed from nonsoluble components and the present polymer solutions or melts include conductive polymer coated housings for sensitive electronic

equipment (microprocessors), infrared and microwave absorbing shields, flexible electrical conducting connectors, conductive bearings, brushes and semi-conducting photoconductor junctions, antistatic materials for packaging electronic components, carpet fibers, waxes for floors in computer rooms and an antistatic spray finisher for plastics, and thin, optically transparent antistatic finishes for CRT screens, aircraft, auto windows and the like.

It is also contemplated to use the present solutions or melts as such as either liquid conductors or liquid semiconductors, much in the manner that liquid mercury is used in various devices. Examples of such devices include gravity switches, fluid level detecting devices or other electrical or electronic switches. Such use is based upon the conductivity of the solution, which the case of polyaniline protonated with DBSA in xylene can represent a relatively high electrical conductivity.

The following specific examples are present to illustrate the invention and are not to be construed as limitations thereon.

#### Example 1

Polyaniline was prepared according to the method described by Y. Cao, A. Andereatta, A.J. Heeger and P. Smith, Polymer, 30 (1989) 2305: A solution of 40 ml of freshly distilled aniline (Aldrich), 50 ml of 35% HCl (Fisher) and 400 ml distilled water was prepared in an 1L Erlenmeyer flask. The flask was placed in a cooling bath maintained at 0°C. Polymerization was effected by addition of an oxidant solution consisting of 46 g of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (Aldrich) and 100 ml of distilled water. After all oxidant was added (2 hr), the flask was capped and left stirring for an additional 3 hours. The

precipitated polymer powder was recovered, filtered and washed with distilled water until the pH of washing liquid was 6-7. Subsequently, the polymer was washed with methanol until the liquid was clear, and then with ethyl ether to eliminate residual water and methanol. Finally, the polymer was dried in a vacuum at room temperature for 48 hours. Emeraldine base form of polyaniline was prepared by compensation of the polyaniline salt. Ten g of polyaniline salt was stirred with 1000 ml of 3%  $\text{NH}_4\text{OH}$  solution during 2 hours at room temperature. The resulting emeraldine base was filtrated and washed by distilled water until the pH of washing liquid was 7-8. Subsequently, the polymer was washed by methanol until washing liquid was colorless and then, with methyl ether. The emeraldine base was dried in dynamic vacuum at room temperature for 48 hours. The resulting polymer was insoluble in all common non-polar or weakly polar solvents, and of high molecular weight; the inherent viscosity of the nonconducting polyaniline measured at 25°C in 97% sulfuric acid, 0.1% w/w, was 1.2 dL/g.

#### Example 2

The nonconductive form of polyaniline as prepared in Example 1, 5.43 g (0.06 M of aniline), was mixed thoroughly with 9.79 g (0.03 M) of p-dodecylbenzene sulfonic acid (DBSA) (Tokyo Kasei) using an agate mortar and pestle in a dry bag filled with nitrogen. The molar ratio of DBSA to aniline repeat unit was 0.5; sufficient to completely protonate the emeraldine base form into the conducting salt form.

## Example 3

Example 2 was repeated with different protonic acids. The electrical conductivity of pressed pellets of the resulting materials are shown in Table 1, together  
5 with the conductivity of the material of Example 2.

Table 1.  
Conductivity ( $\sigma$ ) of emeraldine salt protonated with different protonic acids

10	Acid	$\sigma$ (S/cm)
	<u>Sulfonic acids:</u>	
	H	22
	CH <sub>3</sub>	71
	C <sub>2</sub> H <sub>5</sub>	79
15	C <sub>6</sub> H <sub>13</sub>	10
	C <sub>8</sub> H <sub>17</sub>	19
	CF <sub>3</sub>	10
	C <sub>8</sub> F <sub>17</sub>	4.8
	3-hydroxypropane-	35.5
	(L,D)camphor-	1.8
	(1S)-(+)-camphor-	2.7
	(1R)-(-)-camphor-	2.0
20	dioctylsulfosuccinate	5.8
	benzene-	41
	p-toluene-	22
	4-ethyl-benzene-	17
	m-xylene-4-	1.4
	4-dodecyl-benzene-	26.4
	m-nitrobenzene-	5.4
25	O-anisidine-5-	7.7x10 <sup>-3</sup>
	p-chlorobenzene-	7.3
	p-hydroxybenzene-	6.3
	2,4,5-trichlorobenzene-	1.3x10 <sup>-1</sup>
	aniline-2-	2.0x10 <sup>-2</sup>
	4-nitrotoluene-2-	5.7x10 <sup>-2</sup>
	m-phenylenediamine-	2.0x10 <sup>-3</sup>
30	2-hydroxy-4-methoxy-benzophenone-5-	1.3x10 <sup>-3</sup>
	2-naphthalene-	0.05
	1-diazo-2-naphthalene-4-	
	dinonylnaphthalene-	0.2
	8-hydroxy-5,7-dinitro-2-naphthalene-	8.0x10 <sup>-3</sup>
	4-hydroxy-3-nitroso-1-naphthalene-	2.4x10 <sup>-3</sup>
35	3-pyridine-	1.0x10 <sup>-1</sup>

	8-ethoxyquinoline-5-	$1.3 \times 10^{-5}$
5	polystyrene-p-	0.1
	poly(maleic anhydride-styrene-p-)	$10^{-6}$
	<u>Other:</u>	
	dodecyl sulfate	4
	tetra-n-butylammonium hydrogen sulfate	$2.7 \times 10^{-5}$
10	$C_4F_9COOH$	$4.5 \times 10^{-4}$
	$C_8F_{17}COOH$	2.7
	$C_6F_5OH$	$6.8 \times 10^{-3}$
	$C_6H_5(BOH)_2$	$1.4 \times 10^{-7}$
	bis(2-ethyl hexyl hydrogen phosphate)	7
	diphenyl hydrogen phosphate	1.5

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\* pressed at  $165^\circ C$  for 30 sec.

This example illustrates that polyaniline may be protonated with a great variety of protonic acids.

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## Example 4

The material of Example 2, 0.1 g, was mixed with 0.1 g of DBSA. The mixture was placed into 20 g of xylene; and treated in an ultrasonic bath for 48 hours and subsequently centrifuged. Most of the polyaniline-DBSA complex dissolved to give a deep green solution. Some insoluble solids were removed by decanting.

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## Example 5

The solution of Example 4 was evaporated to yield a solid, which was washed with acetone to remove excess DBSA. The polyaniline-DBSA complex thus obtained was weighed to calculate the content of the conductive polyaniline complex in said solution. Then, Example 2 was repeated but with the additional amount of DBSA varied over the following values: 0 (which is the reference material of Example 2), 0.05, 0.2, 0.3, 0.4, 0.5 g. The concentration of the conducting polyaniline-DBSA complex in said solutions was determined; and plotted against the molar ratio of the total amount of DBSA to PhN in the solution is shown in Figure 1A. These results illustrate that, in order to obtain a soluble conductive polyaniline-DBSA, more than 0.5 equivalents of functionalized protonic acid per aniline repeat unit is necessary. Less than this amount results in a doped, conductive, plasticizable form of the polymer.

## 30 Example 6

Example 5 was repeated, but the initial amount of PANi-DBSA (DBSA/PhN=0.5) salt was 1 g in 10 g of xylene. The solubility of the complex in xylene versus the DBSA/PhN molar ratio is shown in Fig. 1B.

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## Example 7

The material from Example 2 was mixed, in 1 g quantity, with 1 g of additional DBSA to give a molar DBSA/aniline ratio of 1.3. The solubility of the resulting mixture was tested in several different solvents; 0.1 gram of the mixture was placed in 10 g of the various solvents and stirred at room temperature for 1 hr. The results are shown in Table 2.

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Table 2  
Solubility of Polyaniline-DBSA (DBSA/PhN =1.3)  
in Selected Solvents

15	Solvent	Soluble	Dielectric Constant (Room Temperature)
	Toluene	yes	2.4
	1,2,4-Trichlorobenzene	yes	5
20	Chloroform	yes	4.8
	Decalin	yes	2.2
	Xylenes	yes	2.2.-2.6

\*above -80°C.

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Similar results were obtained by repeating the above experiments in Examples 2 and 5 with hexanesulfonic acid and octanesulfonic acid in place of DBSA.

## 30 Example 8

Example 2 was repeated. PANi-DBSA of molar ratio DBSA/PhN=0.5 were mixed with the different plasticizing agents listed in Table 3. The solubility of the PANi-DBSA complex (DBSA/PhN=0.5) in xylene is also

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listed in Table 3. This example illustrated that extra DBSA which was used in Example 5 for dissolution of PANi-DBSA complexes in nonpolar organic solvents can be replaced by wide range of nonacidic additives.

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Table 3. Solubility of DBSA/PhN=0.5 in xylene in the presence of plasticizing additives.

10	Additives(A)	Trade Mark	A/PhN molar ratio	Solubility (%)
	<b>Phenols:</b>			
	4-Hexyloxyphenol $C_6H_{13}OC_6H_4OH$		0.5	0.3
15	3-pentadecylphenol $CH_3(CH_2)_{14}C_6H_4OH$		0.5 0.75	6.8 10.2
	Nonylphenol $C_9H_{19}C_6H_4OH$		0.5	0.2
	4-Dodecylresorcinol		2.0 0.5	7.1 1.4
20			1.0	8.7
	4-(tert-Octyl)phenol $(CH_3)_3C-C_6H_4OH$		1.0 2.0	4.4 7.8
	2,6-Di-tert-butyl-4-methylphenol BHP $[(CH_3)_3C]_2C_6H_2(CH_3)OH$		1.0	0.7
25	3,4- Dimethylphenol $(CH_3)_2C_6H_3OH$		1.0	0.5
	2,6-Dimethylphenol $(CH_3)_2C_6H_3OH$		1.0	1.9
30	<b>Alkyl Sulfonates:</b>			
	Methyl p-toluenesulfonate $CH_3C_6H_4SO_3CH_3$		0.5	2.0
	Ethyl p-toluenesulfonate $CH_3C_6H_4SO_3C_2H_5$		0.5	2.0
	n-Hexyl p-toluenesulfonate $CH_3C_6H_4SO_3C_6H_{13}$		0.5	0.4
35	Ethyl DBSA		0.5	0.6

5	<b>Sulfonamide:</b>			
	Isopropylamine alkylaryl sulfonate $C_{12}H_{25}(C_6H_4)SO_3H-(CH_3)_2CHNH_2$	IPAM	0.5	0.8
10	<b>Alcohols:</b>			
	1-Dodecanol $CH_3(CH_2)_{10}CH_2OH$		0.5	0.2
	1-Tridecanol $CH_3(CH_2)_{11}CH_2OH$		0.5	0.3
	1-Docosanol $CH_3(CH_2)_{20}CH_2OH$		0.5	0.7
15	Ethoxylate $CH_3(CH_2)_xCH_2(OCH_2CH_2)_nOH$ $x=10-14, n=1.3$	Alfonic 1216-22	0.5	0.9
	Ethoxylate $CH_3(CH_2)_xCH_2(OCH_2CH_2)_nOH$ $x=6-8, n=1.0$	Alfonic 810-40	0.5	0.5
20	Ethoxylate $CH_3(CH_2)_xCH_2(OCH_2CH_2)_nOH$ $x=10-12, n=3$	Alfonic 1412-40	0.5	0.9
	Ethoxylate $CH_3(CH_2)_xCH_2(OCH_2CH_2)_nOH$ $x=6-8, n=2$	Alfonic 810-60	0.5	0.4
25	Poly(oxy-1,2-ethanediyl), alpha-(nonylphenoxy)- $\Omega$ -hydroxy $(C_2H_4O)_4C_{15}H_{24}O$	Legpon CO-430	0.5	0.3
	Sulfated alkyl alcohol ethoxylate ammonium salt	Standapol EA-3	0.5	0.5
30				
35				

## Example 9

Examples 2 and 5 were repeated for (+)-10-camphorsulfonic acid (CSA) instead of DBSA. 2,4 and 8 g PANi-CSA complexes (CSA-PhN0.5 and 0.7) were treated in 100 g m-cresol as in Example 2. The PANi-CSA complex dissolved at room temperature to give a viscous deep green solution. Similar results were obtained with the optically active (1S)-(+)-10-camphorsulfonic acid and (1R)-(-)-10-camphorsulfonic acid. This example illustrates that, in contrast to the PANi-DBSA system, extra functionalized protonic acid (i.e., more than 0.5 equivalents of acid per aniline PhN unit) is not necessary in the case of PANi-CSA dissolved in m-cresol. The room temperature solubility of PANi-CSA in various organic solvents are listed in Table 4.

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Table 4. Solubility of PANI-CSA in some organic solvents

5	Solvent	Solubility at room temperature
	m-cresol	⊕
	p-cresol	⊕
	2-ethylphenol	⊕
	2-tert-butylphenol	⊕
10	diisopropylphenol	○
	α',α'',α'''-Trifluoro-m-cresol	⊕
	3-methoxyphenol	○
	2-methoxy-4-methylphenol	○
	xylene(+10% nonylphenol)	○
	xylene(+10% pentadecylphenol)	○
	benzyl alcohol	○
15	3-methylbenzyl alcohol	○
	phenoxyethanol	○
	chloroform	○
	dichloroethane	○
	trichlorobenzene	○

- ⊕ Very soluble; the solubility is more than 10%(w/w).  
 ○ Soluble; the solubility is less 10%(w/w).

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## Example 10

The solubility at room temperature of PANi and selected, functionalized protonic acids was tested in some nonpolar and weakly polar organic solvents. The results are listed in Table 5.

Table 5.

Solubility at room temperature of PANi protonated with various protonic acids with functionalized counter-ions.

Acid	Solubility			
	Decaline	Xylene	CH <sub>3</sub> Cl	m-cresol
<u>Functionalized sulfonic acids:</u>				
C <sub>6</sub> H <sub>13</sub> -	O	O	O	O
C <sub>8</sub> H <sub>17</sub> -	.	O	O	O
C <sub>8</sub> F <sub>17</sub> -	.	.	.	.
4-dodecyl-benzene-	⊕	⊕	⊕	O
(L,D)camphor-	.	.	O	⊕
ethylbenzene-	.	O	O	O
0-anisidine-5-	.	.	.	O
p-chlorobenzene-	.	.	.	O
hydroxybenzene-	.	.	.	O
trichlorobenzene-	.	.	.	O
2-hydroxy-4-methoxy-benzophenone-	.	.	.	O
4-nitrotoluene-2-	.	.	.	O
dinonylnaphthalene-	O	O	O	O
4-morpholineethane-	.	.	.	O
2-[[tris(hydroxymethyl)methyl]amino]-1-ethane-	.	.	.	⊕
<u>Other:</u>				
C <sub>8</sub> F <sub>17</sub> COOH	.	.	.	.
bis(2-ethyl hexyl	.	.	.	.
hydrogen phosphate)	⊕	⊕	⊕	.
diphenyl hydrogen phosphate	O	O	O	.

⊕ Very soluble, the solubility is more than 10%(w/w).

O Soluble, the solubility is less 10%(w/w).

. Soluble in perfluoroalkane, for example, in perfluorodecaline.

## Example 11

A solution was prepared as in Example 4 and was cast onto a glass plate. The xylene was evaporated, and the resulting film was washed with acetone to remove excess DBSA. The remaining film was dried at room temperature and had a four-point probe conductivity of 20 S-cm<sup>-1</sup>.

Similar results were obtained by repeating the above experiment with chloroform, trichlorobenzene, toluene or decaline in place of xylene.

## Example 12

A quantity of 5 g of a solution as prepared in Example 3 was mixed with 0.17 g of ultra-high molecular weight polyethylene (UHMW PE Hostalen GR 412, weight average molecular weight of 2,000,000), 0.01 g of antioxidant and 17.4 ml of xylene and heated in an oil bath at 126.6°C for 1 hour. The resulting hot solution was cast onto an aluminum plate. Xylene was removed by evaporation in air at room temperature. The polyaniline-DBSA complex content was found to 11.8% w/w in the film. Similar experiments were repeated, but the polyaniline-DBSA complex content was varied to be 7.1% and 13.4% w/w, respectively. Part of the films were stretched on a hot plate at 105°C to a draw ratio  $\lambda=40$  ( $\lambda$ =final length divided by initial length). The stretched films had outstanding mechanical properties: Young's modulus in excess of 40 GPa and tensile strength in excess of 2 GPa. The electrical conductivities of unstretched and stretched films, were measured using the standard four-probe method. The results are summarized in Table 6. The use of drawing in this example is an example of the general use of physical distortion of a conductive polymer structure to drastically improve the



physical and electrical properties of the polymer. Any distortion, stretching, drawing or the like in amounts of about a 50% distortion through a 200-fold distortion can be used with advantage.

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Table 6  
Electrical Conductivity of UHMW PE Composite Films  
Containing PANi-DBSA

10	PANi-DBSA content (%)	Conductivity (S-cm <sup>-1</sup> )	
		unstretched	stretched
	7.1	8.4x10 <sup>-4</sup>	2.5x10 <sup>-2</sup>
	11.8	2.9x10 <sup>-1</sup>	3.9
15	13.4	2.9x10 <sup>-2</sup>	11.5

This example demonstrates the feasibility of using this soluble form of conductive polyaniline in the preparation of high-performance polyolefins.

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#### Example 13

Example 12 was repeated, but isotactic polypropylene (M<sub>w</sub> ~100,000 daltons) was used instead of ultrahigh molecular weight polyethylene. The electrical conductivities of the blends was measured by the four-point method and are shown in Fig. 2A.

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#### Example 14

Example 12 was repeated, but with PANi-CSA (CSA/PhN molar ratio = 0.5) in m-cresol, and nylon 4,6 and nylon 12 dissolved in m-cresol were used instead of PANi-DBSA, xylene and ultrahigh molecular weight polyethylene, respectively. Dissolution was carried out at room temperature. The electrical conductivity of the

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blends was measured by the four-point method and is shown in Fig. 2B.

#### Example 15

5 Experiment 14 was repeated. Similar results were obtained with polystyrene, polycarbonates, amorphous nylons, polyacrylonitrile, poly(methylmethacrylate), polyvinylacetate, polyvinylbutyral, polyvinylpyrrolidone, polysulfone and ABS.

10 Table 7 summarizes electrical conductivity data of solution-processed blends with a great variety of insulating polymers.

15 Table 7. Conductivity of solution-processed blends of PANI-functionilized sulfonic acids with various commercial polymers

Host polymer	Acid	Solvent	PANI-salt content in blends of $\sigma=10^{-1}$ S/cm	Conductivity $\sigma$ (S/cm) at weight fraction $\omega$ $\sigma(\omega)$
<b>Homopolymer:</b>				
Polyethylene (PE)	DBSA	xylene, decaline	0.10	5 (0.30) (stretched) 0.1 (0.30) (unstretched)
25 Polypropylene (i-PP)	DBSA	xylene	0.10	10 (0.40)
Polystyrene (PS)	DBSA CSA	CHCl <sub>3</sub> m-cresol	0.20 0.01	1 (0.40) 6 (0.08)
Polybutadiene	DBSA	xylene		3x10 <sup>-6</sup> (0.06)
30 Polysiloxane (Dow Corning RTV 738)	DBSA	xylene		1x10 <sup>-6</sup> (0.02)
Nylon 4.6	CSA	m-cresol	0.07	50 (0.50)
Nylon 12	CSA	m-cresol	0.07	50 (0.50)
35 Zytel 330 (Du Pont, amorphous Nylon)	CSA	m-cresol	0.03	4.8 (0.08)

	Trogamid (Hüls, amorph. Nylon)	CSA	m-cresol	0.04	4.6 (0.08)
5	Polycarbonate(PC)	CSA	m-cresol	0.10	100 (0.60)
	Luran PC	CSA	m-cresol	0.02	32 (0.60)
	Tetramethyl -bis- phenol PC	CSA	m-cresol	0.01	4.8 (0.08)
10	Polyacrylonitril (PAN)	CSA	DMSO		10 <sup>-3</sup> (0.40)
	Poly(methyl metacrylate) ( PMMA)	CSA	m-cresol	0.01	70 (0.15)
		DBSA	CHCl <sub>3</sub>	0.10	10 <sup>-1</sup> (0.10)
	Polyvinylacetate	DBSA	toluene	0.10	10 <sup>-1</sup> (0.20)
		CSA	m-cresol	0.03	50 (0.45)
15	Polyvinylbutyral	CSA	m-cresol	0.03	30 (0.30)
	Polyvinylpyrrolidone	CSA	m-cresol	0.03	1.9 (0.08)
	Polysulfone p-1700	CSA	m-cresol	0.02	5.7 (0.08)
20	<b>Copolymer:</b>				
	ABS	CSA	m-cresol	0.02	26 (0.40)
	Styrolux (polystyrene- butadiene)	CSA	m-cresol	0.03	6.4 (0.088)

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## Example 16

A solution of 4.65 g (0.05 M) of freshly distilled aniline (Aldrich) and 24.48 g (0.075 M) of DBSA and 250 ml xylene was prepared in a 250 ml Erlenmeyer flask. The flask was placed in a bath that was maintained at 25°C. Polymerization was effected by the addition of an oxidant solution containing 4.68 g (0.02 M) of  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (Aldrich) in 20 ml distilled water. After all oxidant was added (over a period of 30 min), the flask was capped and stirring was continued for 24 hours. The molar ratio of oxidant to aniline was 0.4; the monomer concentration was 0.2 M/L; and the ratio of DBSA to aniline was 1.5. A dark green mixture was formed.

The polymer emulsion was poured into 750 ml acetone and the polyaniline-DBSA complex precipitated. This powder was recovered, filtered and washed three times with 150 ml acetone and three times with 150 ml distilled water, and again three times with 150 ml acetone. Finally the powder was dried in a vacuum desiccator for hours at room temperature. The polyaniline-DBS yield was 2.1 g. The DBSA/PhN ratio in the powder was 0.3.

This example illustrates that conductive polyaniline-functionalized protonic acid complexes can be prepared directly from the aniline monomer.

This example further illustrates that one can use a protonic acid to solubilize the aniline in an

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organic solvent and that the solubilized aniline can be subjected to emulsion polymerization, a polymerization technique not available heretofore. In this process, the solvent can be varied as can the protonic acid and the relative proportions of reactants.

#### Example 17

Example 16 was repeated, but the polymerization temperature was 0°C and polymerization time was 96 hours. In general terms, the temperature could be varied over the range of -10°C through 50°C with similar results. Times would vary inversely with temperature.

#### Examples 18-21

Example 16 was repeated, but the molar ratio of DBSA to aniline was, respectively, 4.0, 3.0, 2.0 and 1.0. The experiment could also be repeated substituting other acids for DBSA.

#### Examples 22-25

Example 16 was repeated, but the solvent for the polymerization was, respectively, chloroform (22), toluene (23), decaline (24), 1,2,4-trichlorobenzene (25). Other low dielectric constant nonaqueous liquids could be employed, if desired.

#### Example 26

Example 22 was repeated, but the polymerization temperature was 0°C.

The yields of the above polymerizations were calculated from the ratio of the amount of emeraldine base, recovered after compensation (following the procedure of Example 1), to the amount of initial aniline monomer. The electrical conductivity of the

polyaniline-DBSA complexes of Examples 16-25 were determined by the usual four-probe method at room temperature on pressed pellets. The inherent viscosity (in dL/g) of the polyaniline-DBSA complex and of the emeraldine base obtained after compensation were determined at 25°C in 97 % H<sub>2</sub>SO<sub>4</sub> (0.1% w/w polymer), using an Ubbelohde viscosimeter. The results are presented in Tables 8-10.

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Table 8Effect of Polymerization Temperature

	Example	Temperature	Yield	Conductivity	Viscosity	
		(°C)	(%)	(S-cm <sup>-1</sup> )	(dL/g) complex	base
15	8	25	32.4	3.7	0.99	1.27
	9	0	32.6	1.0	1.21	1.70
	14	25	33.6	0.8	1.26	1.67
20	18	0	36.9	0.5	1.92	2.61

The results in this Table illustrates that it is beneficial to carry out the emulsion polymerization at lower temperatures; it also reveals that the direct preparation of polyaniline-functionalized acid complexes in organic solvents may lead to significantly higher molecular weights of the polymer (cf. Example 1).

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Table 9  
Effect of DBSA/Aniline Ratio

5	Example	DBSA/aniline ratio	Yield (%)	Conductivity (S-cm <sup>-1</sup> )	Viscosity (dL/g)	
					complex	base
	10	4.0	27.2	0.4	0.38	0.61
	11	3.0	37.0	0.2	0.21	0.93
	12	2.0	34.0	0.2	0.24	0.45
10	8	1.5	32.4	3.7	0.99	1.27
	13	1.2	32.6	0.7	0.48	0.68

The results in this Table illustrate that polyaniline-functionalized acid complexes can be prepared directly over a wide range of DBSA/PhN ratios.

Table 10  
Effect of Solvent

20	Example	Solvent	Yield (%)	Conductivity (S-cm <sup>-1</sup> )	Viscosity (dL/g)	
					complex	base
	8	Xylene	32.4	3.7	0.99	1.27
	14	CHCl <sub>3</sub>	33.6	0.8	1.26	1.67
25	15	Toluene	36.7	1.2	1.09	1.35
	16	Decaline	36.8	0.1	1.07	1.18
	17	Tricloro- benzene	33.3	2.0	0.81	1.0 7

The results in this Table illustrate that the polyaniline-functionalized acid complexes can be prepared directly in various non-polar or weakly polar organic solvents.

## Example 27

The mixture of Example 16 was centrifuged at 4000 rpm for 1 hour immediately after termination of polymerization, prior to precipitation of polyaniline with acetone. The soluble part was decanted and washed three times with 400 mL of a 1:1 acetone/water mixture in separation funnel to eliminate excess DBSA and ammonium sulfate. A bright green solution of the polyaniline-DBSA complex in xylene was obtained, which was stable at room temperature during storage. No precipitate appeared during several months. The content of the polyaniline-DBSA complex in the solution was determined by evaporation of the xylene, first in air followed by evacuation in vacuum at room temperature for 24 hours. A typical value of the content was 2% w/w for the polymerization conditions of Example 16.

## Example 28

A mixture was prepared of 0.1 g of the material of Example 16, 0.1 g of DBSA and 20 g xylene was treated in ultrasonic bath overnight. The resulting solution was decanted after centrifugation at 4000 rpm. The concentration of the polyaniline-DBSA complex in the solution was determined as in Example 5. Typically the value of this content was 0.5 % w/w. This example illustrates that the powder of Example 16 can be redissolved in xylene.

Similar results were obtained by repeating the above experiment with chloroform, trichlorobenzene, toluene or decaline (at 90 °C) in place of xylene.

## Example 29

A solution was prepared of 0.1 g of the material of Example 27, 0.1 g of DBSA and 10 g xylene,



according to the method of Example 28. Free standing films of the polyaniline-DBSA complex were obtained by casting from solution and drying at room temperature and subsequent washing with acetone. Typically, the electrical conductivity of the resulting free standing flexible films was ca.  $240 \text{ S-cm}^{-1}$ . Because the protonation level of the films obtained by this procedure was only 0.3, further protonation of the film with 1 M aq. HCl solution increases the conductivity to  $400 \text{ S-cm}^{-1}$ .

This example illustrates that films were produced having values of the electrical conductivity that significantly exceed those commonly reported for polyaniline.

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#### Example 30

Films were prepared of ultra-high molecular weight polyethylene and the polyaniline-DBSA complex, according to the method of Example 12, but the solution of the conductive polyaniline was directly made according to the method of Example 16. The weight ratios of the polyaniline-DBSA complex to the total polymer content were varied from 0.002, 0.01, 0.024, 0.048, 0.09, 0.17, 0.29, 0.34 to 0.35. After drying the electrical conductivity of polyaniline/UHMW PE blend films were determined using the standard four-probe method. The results are given in Figure 3.

The films were stretched on a hot plate at  $105^{\circ}\text{C}$  to a draw ratio of 1:40. The stretched films exhibited a homogeneous distribution of the polyaniline-DBSA complex in the UHMW PE matrix; and high optical anisotropy was observed under the polarizing light. The electrical conductivity of stretched films were determined using the standard four-probe method. In

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comparison with the conductivity of unstretched films, the conductivity after drawing increased by 1-3 orders of magnitude depending on the composition of the films (see Fig. 3). The stretched films had outstanding mechanical properties.

5 This example demonstrates the feasibility of using this soluble form of conductive polyaniline in the preparation of high performance polymer blends of excellent electrical and mechanical properties.

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#### Example 31

A solution was prepared at room temperature of 2.5 g of polystyrene (Polyscience,  $M_w$  125,000-250,000) in 7.5 g chloroform, respectively. A solution of the  
15 conductive polyaniline was directly made according to the method of Example 16; and was added to the polystyrene/chloroform solution in amounts such that the weight ratios of polyaniline-DBSA to polystyrene in the chloroform solutions were 0.011, 0.022, 0.05, 0.1, 0.18,  
20 0.24, 0.39, 0.62, 0.89, respectively. The viscous solutions were cast into films and the chloroform was evaporated in air at room temperature. Surprisingly clear and transparent films were thus obtained. The electrical conductivities of polyblend films were  
25 determined, using the standard four-probe method. The data are shown in Fig. 4.

This example demonstrates the feasibility of using the soluble conductive polyaniline to manufacture conductive articles of outstanding optical clarity.

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#### Example 32

Example 31 was repeated, but the host polymer was the conjugated polymer poly(3-octylthiophene) (Neste Oy,  $M_w$  = 125,000) instead of polystyrene. The weight  
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ratios of polyaniline-DBSA to poly(3-octylthiophene) in the chloroform solutions were 0.032, 0.062, 0.15 and 0.21. The results of electrical conductivity measurements of the polyblend films are also shown in Fig. 4.

#### Example 33

Polybutadiene (Aldrich), 1 g, and benzoylperoxide, 20 mg, were dissolved in 10 g of a polyaniline-DBSA solution in xylene, which was prepared according to the method of Example 16, at room temperature under stirring. A homogeneous solution was obtained which was cast onto a glass substrate. The solvent was removed by evaporation in air at room temperature. The final concentration of polyaniline-DBSA complex in the resulting polyblend film was 6% w/w. This film was cured in an oven at 160°C for 20 minutes. A conductive and very elastic polyaniline-DBSA/polybutadiene rubber film was obtained. The film exhibited an electrical conductivity of  $3 \times 10^{-6}$  S-cm<sup>-1</sup>; the conductivity of the film before curing was  $1 \times 10^{-5}$  S-cm<sup>-1</sup>. The conductive elastomer could reversibly deformed to elongations as much as 600 % without fracture.

#### Example 34

Example 33 was repeated, but silicone rubber (Dow Corning RTV 738) was used in place of polybutadiene. This elastomer was cured at room temperature after evaporation of the xylene. The final concentration of the polyaniline-DBSA complex in the silicone rubber was 1 % w/w. The conductivity of the elastomer was  $1 \times 10^{-6}$

S-cm<sup>-1</sup>. The above Examples 33 and 34 demonstrate that, with the soluble polyaniline, conductive articles can be manufactured having outstanding elastomeric properties.

5     Example 35

The material of Example 2, in 2.66 g quantity, was mixed with 17.7 g of xylene (13% w/w) in an ultrasonic bath. After 2 hours a stable emulsion of the polyaniline-DBSA in xylene was obtained.

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Example 36

Films were prepared of ultra-high molecular weight polyethylene and the polyaniline-DBSA complex, according to the method of Example 12, but in place of the solution prepared according to the method of Example 27, the emulsion of Example 35 was used. The weight ratios of the polyaniline-DBSA complex to the total polymer content were varied from 0.42, 0.50, 0.60 and 0.70. After drying the electrical conductivity of the polyaniline/UHMW PE blend films were determined using the standard four-probe method. The results are given below in Table 11.

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Table 11  
Electrical Conductivity of UHMW PE Composite  
Films Containing PANi-DBSA

	PANi-DBSA content (%)	Conductivity (S-cm <sup>-1</sup> )
5	20.1	0.3
	42.0	0.1
	60.0	1.2
10	70.0	2.0

15 This experiment shows that polyblend systems with a large content of the conductive polyaniline can be prepared.

Example 37

20 The conductive form of polyaniline was prepared as in Example 2. Differential scanning calorimetry (DSC) scans of the material exhibited an exothermal peak at ca. 95°C and an endothermal peak at ca. 150°C. The thermal stability of EB-DBSA complex was examined by thermogravimetric (TG) analysis (Mettler TA3000 system). The complex was stable at temperatures exceeding 270°C.

25 Using a laboratory press at room temperature, the resulting mixture was pressed into a pellet at room temperature. After pumping for 96 hours in dynamic vacuum at room temperature, the electrical conductivity of the pellet of the polyaniline-DBSA complex was

30 measured in a dry box filled with argon, using the standard four-probe method. The resulting conductivity was 26.4 S-cm<sup>-1</sup>.

Remarkably it was observed that a coherent thin film was obtained by pressing at 160 °C, which is

indicative of the plasticizing effect of the functionalized protonic acid. After pumping for 96 hours in dynamic vacuum at room temperature, the electrical conductivity of the film of the polyaniline-DBSA complex was measured in a dry box filled with argon. The resulting conductivity was as high as  $92 \text{ S-cm}^{-1}$ . This example shows how a fluid phase protonic acid such as DBSA can itself serve as a solvent/plasticizer. The acid can be fluid (liquid or semisolid) at room temperature or at an elevated temperature and achieve the advantages of the invention.

#### Example 38

The nonconductive form of polyaniline of Example 1, 0.091 g (0.001 M), was mixed in an Agate mortar and pestle with 0.163 g DBSA (0.0005 M) and 0.254 g of powdery linear polyethylene (GR 2755;  $M_w=200,000$ ) in a dry bag filled with nitrogen. The mixture was pressed at  $165^\circ\text{C}$  between hot plates for 30 seconds; the 30 second hot-processing step was repeated three more times (for a total of four) to assure uniform mixing. Flow and mixing were observed to occur and tough and flexible films were obtained after cooling to room temperature. The weight ratio of the polyaniline-DBSA (DBSA/PhN=0.5) complex to the total polymer was 0.5.

#### Example 39

Example 38 was repeated, but the amount of polyethylene was varied such that the weight ratio of the polyaniline-DBSA complex to the total polymer was 0.34, 0.20 and 0.11. Flow and mixing were observed to occur and tough and flexible films were obtained after cooling to room temperature. This example shows that in

situations where the acid is fluid and serves as the liquid (solvent) phase one can additionally add a wide range of other polymers and achieve the desired conductivity properties.

5

#### Example 40

The electrical conductivities of the materials of Examples 38-39 were measured using the standard four-probe method. The results are shown in Figure 5.

10

These data show that this conductive form of polyaniline can be mixed in the melt with polyolefins to yield materials of excellent electrical and mechanical properties. The Examples 38-39 also show that molten polymers can be used as plasticizing liquids, and that additional amounts of the functionalized protonic acid can increase the conductivity through enhanced miscibility between the conductive polyaniline and polyethylene.

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#### 20 Example 41

Examples 38 and 39 were repeated, but in place of polyethylene powdery nylon 12 (Polysciences) was used. The mixture was pressed at 175°C between hot plates for 30 seconds and subsequently re-pressed (again for 30 seconds). Flow and mixing were observed to occur and tough and flexible films were obtained after cooling to room temperature. The electrical conductivities of the films were measured using the four-probe method; the results are shown in Figure 6.

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This shows that this conductive form of polyaniline can be mixed in the melt with nylons to yield materials of excellent electrical and mechanical properties. It also shows that molten polymers and

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liquid protonic acids can be used as plasticizing liquids.

#### Example 42

5           Example 38 and 39 were repeated, but in place of polyethylene poly(vinylchloride) (PVC) power was used. The mixture was pressed at 165°C between hot plates. In separate experiment plasticizer Mesamoll (Bayer) was used instead of additional DBSA. The electrical conductivity  
10 of the resulting tough and flexible films were measured using the four-probe method; the results are shown in Figure 7.

          Example 42 shows that neutral plasticizers can be used in combination with DBSA as plasticizing liquid  
15 for melting processing of PANi polyblends to yield materials of excellent electrical and mechanical properties.

#### Example 43

20           Example 42 was repeated, but in place of DBSA, 0.33 mole DOHP was used per PhN repeat unit. The mixture was pressed at 165°C between hot plates. The electrical conductivity of the resulting tough and flexible films were measured using the four-probe method; the results  
25 are shown in Figure 8.

          Example 42 shows that phosphates can be used as functionalized protonic acid for rendering PANi  
conductive and plasticizing and mixing with PVC to yield materials of excellent electrical and mechanical  
30 properties.

          In some embodiments these materials take advantage of their transparency and/or their coloration to give rise to transparent or colored electrodes. In addition, in some embodiments the transparent or colored  
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electrodes are employed in flexible light-emitting diodes. The following examples relate to these embodiments.

5     Example 44

Emeraldine base, 1.092 g, characterized in terms of molecular weight and the like by having an inherent viscosity of 1.2 dL/g when measured at room temperature as a 0.1% w solution in 97% H<sub>2</sub>SO<sub>4</sub>, (.012M),  
10     was mixed with 1.394 g of CSA, ( $\pm$ )-10-camphorsulfonic acid, (Aldrich) using an agate mortar and pestle in inert atmosphere (i.e. in a glove-bag filled with nitrogen gas). The molar ratio of CSA to aniline repeat unit was 0.5. A quantity (1.275 g) of the resulting mixture was  
15     placed into 61.0 g of m-cresol, treated in an ultrasonic bath for 48 hours, and subsequently centrifuged. Most of the polyaniline-CSA complex dissolved to give a viscous deep green solution. Minor insoluble solids were removed by decanting. Part of the solution was set aside,  
20     weighed, and then cast onto a glass slide. After evaporation of the solvent, a flexible free-standing film was obtained; the film was weighed to calculate the content of the conductive polyaniline complex in said solution. The concentration was determined as 1.94% (w/w).

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Example 45

Example 44 was repeated, but with the CSA/PhN ratio varying over the following values: 0.6, 0.7, 0.8, 0.9, 1.0, 1.5, 2.0. To make the polyaniline-CSA  
30     solution. 0.138, 0.152, 0.166, 0.180, 0.194, 0.264, 0.334, g of each mixture were added into 10 g of m-cresol to keep the emeraldine content in each solution at 0.0006 M in 10 g m-cresol. Complexes with CSA/PhN molar ratio equal or larger than 0.7 were completely soluble in  
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m-cresol; thus centrifuge separation was not necessary for such solutions. Free-standing polyaniline films were obtained from all those solutions after casting onto glass slides and solvent evaporation. The resulting films were washed by acetone several times. During this process, most of excess CSA was removed from film, as was evident from the results of the compensation procedure. The compensation was done as follows: in each case, a small weighed piece of said free-standing PANi/CSA film was treated by 3% aq.  $\text{NH}_4\text{OH}$  solution for two hours. The resulting neutral PANi (emeraldine base) films were washed with water and acetone. After drying in air, the films were weighed again. From the difference in weight before and after compensation, the content of CSA in the films was calculated as summarized in Table 12. The conductivities of the conducting PANi/CSA films were determined by the usual four probe method, in air, and are also listed in Table 12.

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Table 12Conductivity of Free-Standing Polyaniline-CSA Film

	<u>CSA/PhN Ratio</u>		Conductivity <u>S-cm<sup>-1</sup></u>
	<u>Initial in Solution</u>	<u>in Film</u>	
25	0.5	0.49	230
	0.6	0.53	163
	0.8	0.51	168
	0.9	0.53	138
	1.0	0.54	158
30	1.5	0.58	143
	2.0	0.58	154

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## Example 46

Homogeneous and transparent PANi/CSA thin films were obtained when the solution of Example 44 was spin cast (10000 rpm, 2 min) onto glass or sapphire substrates. The surface resistivity of spin cast PANi/CSA thin film (ca. 0.55  $\mu\text{m}$ ) on glass substrate was 166 ohms/square as determined by the four probe method. The surface resistivity of spin cast PANi/CSA thin film (ca. 1.4  $\mu\text{m}$ ) on glass substrate was 66 ohms/square as determined by the four probe method. Fig. 9 shows the transmission spectra of the three PANi/CSA films (ca. 0.2  $\mu\text{m}$  thickness, 0.55  $\mu\text{m}$  thickness and 1.4  $\mu\text{m}$  thickness) on a glass substrate. In the visible region the transmittance was 70-80% for the 1.4  $\mu\text{m}$  thick film, 75%-85% of the 0.55  $\mu\text{m}$  film and 80%-90% of the 0.2  $\mu\text{m}$  film. This example demonstrates that conductive transparent films of the polyaniline complex can be cast from solution.

## Example 47

A one (1) gram quantity of solution, prepared as in Example 44, was mixed with one (1) gram of 10%(w/w) solution of poly(methyl methacrylate), PMMA in m-cresol. The resulting homogeneous solution was spin-cast (10000 rpm, 2 min) onto a glass substrate. Subsequently, the substrate was put on a hot plate at 50 °C, in air, to remove the remaining m-cresol from the film. The PANi/CSA complex content was 16.2% w/w (PANi/CSA to total polymer) in the film. Transparent free-standing blend films with said composition were prepared with thickness in the range 20-30  $\mu\text{m}$  by casting the corresponding solution onto a glass slide. Similar experiments were repeated, but the polyaniline-CSA complex content was varied to be 75%, 66%, 54.8, 43.7%, 28.0%, 20.6%, 8.8%, 3.7%, 1.9%, 0.96%, 0.48%, and 0.24%. The surface

resistance for the thin films on substrates and the bulk conductivity for the free-standing films were measured using the standard four-probe method; the conductivity results are summarized in Fig. 10.

5            Fig. 11 shows the transmission spectra of the thin spin-cast films for PANi-CSA ratio of 16.2%, 8.8% and 3.7%, respectively. The surface resistance was  $6.3 \times 10^3$ ,  $4.5 \times 10^4$ , and  $1.6 \times 10^5$  ohms/square, respectively. All of the spin-cast thin films exhibit transmission  
10 greater than 90% throughout the visible region of the spectrum. Increasing the thickness of the film leads to a decrease in surface resistance, as expected. Fig. 12 compares the transmission spectra of spin cast (onto glass substrates) films of different thickness with  
15 polyaniline-CSA content 20.6%. The thickest of these films (approx.  $2.1 \mu\text{m}$ ) of polyaniline-CSA complex with PMMA film exhibited excellent transparency in the visible region of the spectrum and a low surface resistance (130 ohms/square). Data for a number of free standing cast  
20 films (with thickness around 45-65  $\mu\text{m}$ ) are summarized in Fig. 13. This example demonstrates that conductive transparent films of the polyblends containing polyaniline complex at different concentrations in PMMA can be cast from solution.

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#### Example 48

Example 47 was repeated, but with the CSA/aniline ratio fixed at 0.7; the polyaniline-CSA complex content was varied as follows: 43.6%, 27.8%,  
30 13.4%, 7.2%, 3.72%, 1.9% and 0.96%, respectively. The bulk conductivity data for free-standing film are plotted in Fig. 10. Spin cast films exhibit excellent visible light transmission; two representative spectra are shown in Fig. 14. This example demonstrates that conductive  
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transparent films of the polyblends containing polyaniline complex at different concentrations in PMMA can be cast from solution.

5    Example 49

Emeraldine base (2.18 g, 0.024M of PhN) was mixed thoroughly with 3.91 g (0.12 M) of p-dodecylbenzenesulfonic acid (Tokyo Kasei) using an agate mortar and pestle in a glove bag filled with nitrogen. The  
10    molar ratio of DBSA to PhN repeat unit was 0.5. A solution of polyaniline/DBSA complex in chloroform was prepared by mixing of 0.2 g of the resulting polyaniline/DBSA complex with 0.2 g of additional DBSA and 20 g of chloroform. The mixture was treated in an  
15    ultrasonic bath for 24 hours and subsequently centrifuged. Insoluble solids were removed by decanting. The concentration of polyaniline/DBSA complex in the solution was 1.16%(w/w) as determined by weight change before and after removing solvent from a previously  
20    weighed solution. A 0.5 gram quantity of the resulting solution was mixed with 0.5 gram of 10%(w/w) solution of poly(methyl methacrylate), PMMA in chloroform. The resulting homogeneous solution was cast onto a glass slide to obtain a transparent freestanding film. The  
25    PANi/DBSA complex content in the film was 10.4% w/w (PANi/DBSA to total polymer). Similar experiments were repeated, but the polyaniline-DBSA complex content was varied to be 5.5%, 2.3%, 1.2%, 0.6%, 0.3%, 0.1%. Conductivity data measured by the four probe technique  
30    are shown in Fig. 15. All these films exhibit good transparency in the visible region.

## Example 50

Example 48 was repeated, using polyvinylacetate (PVAc) as the host polymer. The initial concentration of PVAc in m-cresol was 5% w/w. The bulk conductivity data are shown in Fig. 16. Spin cast films exhibit excellent visible light transmission; the spectra are shown in Fig. 17. This example demonstrates that conductive transparent films of the polyblends containing polyaniline complex at different concentrations in PVAc can be cast from solution.

## Example 51

Example 48 was repeated, using a polycarbonate (PC) as the host polymer. The initial concentration of PC in m-cresol was 4.74% w/w. The polyaniline-CSA complex content in the blend films was 62.0%, 44.9%, 23.6%, 14.0%, 7.3%, 3.8% and 2.0%, respectively. The electrical conductivity of resulting transparent free-standing blend films is shown in Fig. 18. This example demonstrates that conductive polyblend films of PANi-CSA with PC can be cast from solution.

## Example 52

Example 47 was repeated, using poly(acrylonitrile) (PAN) as the host polymer. The PAN and polyaniline-CSA complex were dissolved in dimethylsulfoxide (DMSO) by stirring at room temperature to get solutions with concentrations 2%, 3.7%, respectively. The polyaniline-CSA complex content in resulting blend film was 31.9%, 15.6%, 8.6%, and 4.7%, respectively. The electrical conductivities of resulting free-standing blend films are shown in Fig. 19. The films exhibited excellent transparency in visible region, similar to those shown in Fig. 12 for PMMA blends. This

example demonstrates that conductive polyblend films of PANi-CSA with PAN can be cast from solution.

#### Example 53

5           Example 47 was repeated, using Styrolux (a block co-polymer of polystyrene-butadiene; BASF), aromatic polyethersulfone, tetramethyl-bis-phenol A polycarbonate, Zytel 330 (amorphous Nylon; DuPont), Trogamid (amorphous Nylon; Hüls), polyvinylpyrrolidone  
10 (Polysciences), polystyrene (Polysciences), poly(styrene-acrilonitrile) (BASF) as host polymers. The polyaniline-CSA complex content in the resulting blend films were 8.8%, 4.6% and 0.96%. For all these polymers, optically transparent films were obtained. The bulk  
15 electrical conductivities of free-standing films are listed in Table 13. Spin cast film exhibit similar transmission spectra as shown in Fig. 20. This example demonstrates that conductive transparent films of the polyblends containing polyaniline complex at different  
20 concentrations in a wide variety of host polymers can be cast from solution.

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Table 13  
Conductivity of Blend Films of Polyaniline-CSA  
Complex with Several Commercial Polymers

5	<u>Polymer</u>	<u>Conductivity (S-cm<sup>-1</sup>)</u>		
		<u>8.8%</u>	<u>4.6%</u>	<u>0.96%</u>
	Styrolux	6.4	2.2	.02
	Aromatic polyether sulfone	5.7	2.8	.07
10	tetramethyl-bis-phenyl A polycarbonate	2.0	.42	.43
	Zytel 330	4.9	.63	.01
	Trogamid	4.6	.73	.003
	polyvinylpyrrolidone	1.4	1.0	.02
	polystyrene	6.0	2.0	.12
15	poly(styrene-acrylonitrile)	6.4	2.4	.14

#### Example 54

Flexible LEDs were formed using the materials of this invention. Polyaniline films were spin-cast from solution in the conducting emeraldine salt form, for use as the transparent, flexible, hole-injecting electrode, onto a free-standing poly(ethylene terephthalate) (PET) film as substrate. Prior to use as the substrate, the PET free standing film substrate was cleaned by boiling in an acetone/isopropanol mixture and subsequently dried at 80°C for 1 hour.

A polyaniline solution was prepared using the method of Example 44 and spin-coated onto the PET substrate film.

After spin-coating, the PANi/PET structures were dried at 60°C for 12 hours. A layer of poly(methoxyhexyloxyphenylenevinylene) (MEH-PPV) was then



deposited onto the PANi surface by spin-coating from a 0.5% (wt/wt) solution of MEH-PPV in xylenes.

- No sign of dissolution of the PANi from the MEH-PPV solution could be observed. The two component system was designed so that each component, the PANi-CSA complex and MEH-PPV, were separately soluble; but each was insoluble in the solvent which dissolved the other.

Calcium was used as the electropositive metal to serve as the rectifying and electron-injecting top contact. The calcium was deposited by vacuum evaporation at a pressure below  $10^{-6}$  Torr.

The deposition of the MEH-PPV layer and all physical measurements of the LED devices were carried out in nitrogen atmosphere in a controlled atmosphere dry-box. Contact to PANi was made by a thin, vacuum evaporated gold film. The gold contact was used in the initial studies to make certain that the PANi electrode was not current limiting; however, subsequent experiments have shown that it is also possible to contact the transparent PANi electrode with silver paste or, simply, with an alligator clip. A diagram of the structure of the flexible "plastic" LED is shown in Figure 21.

The PANi electrode has a light green color since it has a transmission window extending from about 475 nm into the infrared. The absorption spectrum of the PANi electrode (Figure 22) shows the characteristic features of the emeraldine salt form of polyaniline with a strong absorption peak at 440 nm and a broad absorption band extending into the infrared. The electroluminescence from the semiconducting MEH-PPV active layer falls right in the transmission window between the two principal absorptions of the PANi electrode.

The "plastic" LED is flexible and can be curled and bent (even folding back on itself in a sharp 180° bend) without failing, as would occur with conductors of the art. The robust nature of the four-layer structure clearly proves the excellent mechanical adhesion of the PANi/MEH-PPV heterostructure interfacial contact and the PANi/PET contact (and, in addition, of the Ca/MEH-PPV contact).

The current-voltage (IV) characteristic (Figure 23) of the device exhibits rectifying behavior. Above 1.8 V, in the voltage range where the LED devices start to emit light, the current through devices utilizing the conducting PANi transparent film as the hole-injecting contact are almost the same as in devices fabricated with ITO as the hole-injecting contact.

The quantum efficiency of the device of this example is approximately 1% (photons out per electron in). The light emitted by the device is easily visible under ordinary room lighting even at low bias voltages (3-4 volts) (Figure 24).

#### Example 55

Transparent conducting films of the PANi-CSA complex used in Example 54 were spin coated with a variety of thicknesses; the thickness and, accordingly, the surface resistance of the PANi/PET electrode can be controlled by varying the spinning speed and/or the concentration of the PANi solution. This also affects the transmittance of the PANi film as can be seen in Figure 9 which shows the transmittance of visible light between 475-675 nm for PANi films with three different thicknesses and, therefore, three different surface resistance values.

The PANi coated PET electrode is mechanically flexible and robust; it can withstand repeated sharp bends back and forth without loss of surface conductance. This is in contrast to ITO coated PET electrodes which are delicate and easily cracked with consequent loss of conductivity.

The conducting PANi film makes an excellent ohmic contact to p-type semiconducting polymers.

#### 10 Example 56

A light emitting diode was fabricated on a glass fiber (50 micron diameter) using the following procedure:

Step 1: After cleaning the glass fiber, the fiber was dipped into a solution of polyaniline/CSA in m-cresol (Example 44) to a depth of about five centimeters. After extracting the fiber from the solution, a PANi/CSA film suitable for use as a hole injecting contact was on the surface of the fiber. The PANi film was dried at 60°C for 1 hour.

Step 2: The portion of the glass fiber with the PANi film was then dipped into a solution of MEH-PPV prepared according to Example 54. When dipping the PANi-coated fiber to form the MEH-PPV layer, care was taken to leave a small length of the PANi film exposed to facilitate electrical contact to the PANi hole-injecting electrode.

Step 3: Calcium was used as the electropositive metal to serve as the rectifying and electron-injecting top contact. The calcium was deposited onto the fiber by vacuum evaporation at a pressure below  $10^{-6}$  Torr.

The resulting flexible LED on the fiber end can be bent without failing. The current-voltage (I-V)

characteristic of the device exhibits rectifying behavior. The quantum efficiency of the device of this example is approximately 1% (photons out per electron in). The light emitted by the device is easily visible under ordinary room lighting even at low bias voltages (3-4 volts).

A special feature of the flexible LED fabricated directly onto a glass fiber is that the light from the LED is guided down the fiber by internal reflection such that a bright emission is evident at the ends of the fiber.

#### Example 58

The fiber LED of Example 57 was placed across a metal rod (10 mm diameter) heated at 90°C. The fiber was allowed to heat up and subsequently bent over the rod. The bent LED was cooled to room temperature and retained its curved shape and its light emitting characteristics.

This example illustrates that LEDs supported on thermoplastic substrates (rods, fibers, films, sheets, etc.) can be post-molded by common heat treatment procedures used in the polymer industry.

#### Example 59

Adhesive glue was applied to the flexible LED of Example 54. The structure was then affixed to a curved surface while retaining its light emitting characteristics.

This example shows that the flexible LEDs can be used in a variety of applications where attachment to flexible curved surfaces is critical, such as labels, signs, etc.

## Example 60

Example 54 was repeated, with the electron-injecting calcium contact replaced by polyquinoline, a semiconducting polymer which has been characterized as n-type. The polyquinoline film was spun from solution in formic acid (1% polyquiniline by weight). The electrical contact to the polyquinoline was made with a gold film vapor deposited onto the polyquinoline layer.

Since MEH-PPV has been characterized as a p-type polymer, the resulting structure forms a pn heterojunction. The all-polymer pn heterojunction was electrically characterized as a rectifying diode; rectification ratio  $10^3$  at 5 volts bias, turn-on voltage of 2 volts, and forward resistance (in the linear regime) of 200 ohms.

Light emission was observed at under forward bias at voltages in excess of 60 volts.

Examples 54-60 illustrate in specific embodiments the general aspect of this invention of providing flexible LEDs. These flexible LEDs include the following layers in their structure, all of which are flexible--that is, capable of being bent by at least  $15^\circ$  without fracturing. Typically, but optionally, they include a solid flexible transparent polymer support. This can be selected broadly from any flexible polymer such as poly(ester), poly(olefin), poly(aramide), poly(acrylate), methacrylate, poly(carbonate), or the like. The function of this support is to add structural body to the LED. This support is not conductive. In Figure 21, this layer is shown as "PET." In cases where the other layers of the LED are themselves robust, this support layer could be omitted. If present, the layer can be of any thickness. The next layer is the conducting hole-injecting electrode. This layer includes

a PANi material as described herein. It can be PANi alone or in admixture with other polymers. The layer should have a low resistance--i.e., less than 300 ohms per square and preferably less than 100 ohms per square.

5 These resistances are generally achieved with thicknesses of from about 50 nm to a few (up to 10) microns. Thicker or thinner layers can be used if the desired low resistance is achieved. This layer can be cast or otherwise formed as described hereinabove.

10 An electrical contact is made to the PANi layer. We have used gold but any method of establishing electrical contact will work.

The third layer in the LED structure is the electroluminescent layer made up of conjugated polymer.  
15 The conjugated polymers used herein include soluble conjugated polymers known in the art. These include, for example, poly(2-methoxy,5-(2'-ethyl-hexyloxy)-p-phenylenevinylene) or "MEH-PPV", P3ATs, poly(3-alkylthiophenes) (where alkyl is from 6 to 16 carbons),  
20 such as poly(2,5-dimethoxy-p-phenylene vinylene) - "PDMPV", and poly(2,5-thienylenevinylene); poly(phenylenevinylene) or "PPV" and alkoxy derivatives thereof; and polyanilines.

The conjugated polymer can be deposited or cast  
25 directly from solution. The solvent employed is one which will dissolve the polymer and not interfere with its subsequent deposition. It should also be selected to not dissolve the PANi layer already laid down.

Typically, organic solvents are used for the  
30 conjugated polymer solution. These can include halohydrocarbons such as methylene chloride, chloroform, and carbon tetrachloride, aromatic hydrocarbons such as xylene, benzene, toluene, other hydrocarbons such as decaline, and the like. Mixed solvents can be used, as  
35

well. Polar solvents such as water, acetone, acids and the like may be suitable. These are merely a representative exemplification and the solvent can be selected broadly from materials meeting the criteria set forth above.

When depositing the conjugated polymer on the PANi layer, the solution can be relatively dilute, such as from 0.1 to 20% w in concentration, especially 0.2 to 5% w. Film thicknesses of 50-400 and 100-200 nm are used.

In some embodiments, the conjugated polymer is present in admixture with a carrier polymer.

The criteria for the selection of the carrier polymer are as follows. The material should allow for the formation of mechanically coherent electroluminescent films, at low concentrations, and remain stable in solvents that are capable of dispersing, or dissolving the conjugated polymers for forming the final film. Low concentrations of carrier polymer are preferred in order to minimize processing difficulties, i.e., excessively high viscosity or the formation of gross inhomogeneities; however the concentration of the carrier should be high enough to allow for formation of coherent structures. Preferred carrier polymers are flexible chain polymers, such as polyethylene, isotactic polypropylene, polyethylene oxide, polystyrene, and the like. Under appropriate conditions, which can be readily determined by those skilled in the art, these macromolecular materials enable the formation of coherent structures from a wide variety of liquids, including water, acids, and numerous polar and nonpolar organic solvents.

Selection of the carrier polymer is made primarily on the basis of compatibility of the conjugated

polymer, as well as with the solvent or solvents used.

The initial concentration of the carrier polymer generally is selected above 0.1% by volume, and more preferably above about 0.75% by volume. On the other hand, it is not desirable to select carrier polymer concentrations exceeding 90% by volume, because this has a diluting effect on the final conjugated polymer composite product. More preferably, the concentration of the carrier polymer in the solution is below 50% by volume.

The solvent system for depositing conjugated polymer and carrier polymer should also be one and will not interfere with the previous layers or the subsequent structure formation process.

15

#### The Electron Injecting Contact

The final layer of the LED structure which is located on the other side of the conjugated polymer film from the PANi layer is an electron-injecting contact. This is fabricated from a low work function metal or alloy (a low work function material has a work function below 4.3. Typical materials include indium, calcium, barium and magnesium, with calcium being a particularly good material. These electrodes are applied by using methods well-known to the art (e.g. evaporated, sputtered, or electron-beam evaporation) and acting as the rectifying contact in the diode structure.

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What is claimed is:

1. A conductive polymeric composition comprising a nonconductive or semiconductive substrate  
5 having intimately mixed therewith polyaniline of film-forming molecular weight in admixture with an effective protonating amount of a protonic acid, the counter-ion of said protonic acid being functionalized so as to be compatible with the substrate and forming a complex with  
10 the polyaniline that imparts conductivity to the polymeric composition.

2. The conductive polymeric composition of claim 1 wherein the substrate has a dielectric constant  
15 below 22 and the polyaniline complex has a conductivity greater than about  $10^{-3}$  S-cm<sup>-1</sup>.

3. The conductive polymeric composition of claim 2 wherein the substrate is nonpolar or weakly  
20 polar.

4. The conductive polymeric composition of claim 2 wherein the substrate comprises a solvent in which the functionalized counter-ion is soluble.  
25

5. The conductive polymeric composition of claim 2 wherein the substrate comprises a bulk polymer with which the functionalized counter-ion is compatible.

30 6. The conductive polymeric composition of claim 2 wherein the substrate comprises a bulk polymer and a solvent, with both of which the functionalized counter-ion is compatible.

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7. The conductive polymeric composition of claim 2 comprising at least about 10% by weight of substrate and having a microstructure comprising a continuous phase comprising the polyaniline and the protonic acid with said functionalized counter-ion.

8. The conductive polymeric composition of claim 2 comprising sufficient polyaniline and functionalized protonic acid to provide a protonated polyaniline having a conductivity of at least about  $10^{-1}$  S-cm $^{-1}$ .

9. The conductive polymeric composition of claim 2 comprising sufficient polyaniline and functionalized protonic acid to provide a protonated polyaniline having a conductivity of at least about  $3 \times 10^2$  S-cm $^{-1}$ .

10. The conductive polymeric composition of claim 2 wherein the polyaniline is polyaniline having a weight average molecular weight of greater than about 10,000 prepared by polymerizing an aniline of Formula 1:



wherein:

30 n is an integer from 0 to 4;

m is an integer from 1 to 5 with the proviso that the sum of n and m is 5;

R is the same or different at each occurrence and is alkyl, alkenyl, alkoxy, cycloalkyl, cycloalkenyl,

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alkanoyl, alkylthio, aryloxy, alkylthioalkyl, alkylaryl,  
 arylalkyl, alkylsulfinyl, alkoxyalkyl, alkylsulfonyl,  
 aryl, arylthio, arylsulfinyl, alkoxycarbonyl,  
 arylsulfonyl, carboxylic acid, halogen, cyano, or alkyl  
 5 substituted with one or more sulfonic acid, carboxylic  
 acid, halogen, nitro, cyano or epoxy moieties; or any two  
 R substituents taken together are an alkylene or  
 alkenylene group completing a 3, 4, 5, 6 or 7-membered  
 aromatic or alicyclic carbon ring, which ring may include  
 10 one or more divalent heteroatoms of nitrogen, sulfur,  
 sulfinyl, sulfonyl or oxygen.

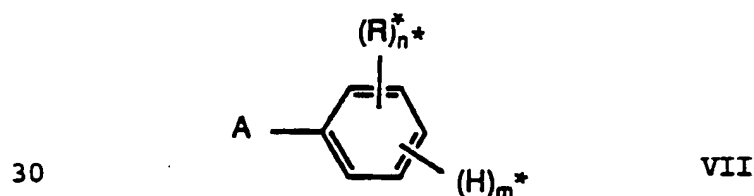
11. The conductive polymeric composition of  
 claim 10 wherein m is equal to 5 and n is 0 such that the  
 15 aniline is unsubstituted aniline.

12. The conductive polymeric composition of  
 claim 10 wherein n is greater than 0 such that said  
 polyaniline is derived from substituted aniline.

20

13. The conductive polymeric composition of  
 claim 3 wherein the counter-ion is of the Formula VI-VII:

25 or  $A-R_1$  VI



wherein:

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A is sulfonic acid, selenic acid, phosphonic acid, a carboxylic acid, hydrogen sulfate, hydrogen selenate, or hydrogen phosphate;

$n^*$  is an integer from 0 to 5;

5  $m^*$  is an integer from 1 to 4 with the proviso that the sum of  $n^*$  and  $m^*$  is 5;

$R_1$  is alkyl, alkenyl, alkoxy, alkanoyl, alkylthio, alkylthioalkyl, having from 5 to about 20 carbon atoms; or arylalkyl, alkylsulfinyl, 10 alkoxyalkyl, alkylsulfonyl, alkoxycarbonyl, carboxylic acid, where the alkyl or alkoxy has from 0 to about 20 carbon atoms; or alkyl having from 3 to about 20 carbon atoms substituted with one or more sulfonic acid, carboxylic acid, halogen, nitro, cyano, diazo, or epoxy 15 moieties; or a substituted or unsubstituted 3, 4, 5, 6 or 7 membered aromatic or alicyclic carbon ring, which ring may include one or more divalent heteroatoms of nitrogen, sulfur, sulfinyl, sulfonyl or oxygen such as thiophenyl, pyrrolyl, furanyl, pyridinyl; or a polymer 20 backbone to which a plurality of A units are attached.

$R^*$  is the same or different at each occurrence and is alkyl, alkenyl, alkoxy, cycloalkyl, cycloalkenyl, alkanoyl, alkylthio, aryloxy, alkylthioalkyl, alkylaryl, arylalkyl, alkylsulfinyl, alkoxyalkyl, alkylsulfonyl, 25 aryl, arylthio, arylsulfinyl, alkoxycarbonyl, arylsulfonyl, carboxylic acid, halogen, cyano, or alkyl substituted with one or more sulfonic acid, carboxylic acid, halogen, nitro, cyano, diazo or epoxy moieties; or any two R substituents taken together are an alkylene or 30 alkenylene group completing a 3, 4, 5, 6 or 7 membered aromatic or alicyclic carbon ring or multiples thereof, which ring or rings may include one or more divalent heteroatoms of nitrogen, sulfur, sulfinyl, sulfonyl or oxygen.

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14. The conductive polymeric composition of claim 13 wherein A is sulfonic acid.

5           15. The conductive polymeric composition of claim 14 having the formula VII wherein  $m^*$  is 4 and  $n^*$  is 1 and the counter-ion includes  $R^*$ , which is the same or different at each occurrence and is alkyl, alkenyl or alkoxy, having from 2 to about 14 carbon atoms or alkyl  
10 substituted with one or more carboxylic acid, halogen, nitro, cyano or epoxy moieties.

          16. The conductive polymeric composition of claim 13 comprising polyaniline plus one or more  
15 aprotonic acids selected from the group consisting of sulfonic acids  $\text{HOSO}_2\text{-R}_1$ , where  $\text{R}_1$  is selected from the group consisting of  $\text{C}_6\text{H}_{12}\text{-}$ ,  $\text{C}_8\text{H}_{17}\text{-}$ ,  $\text{C}_8\text{F}_{17}\text{-}$ , 4-dodecylbenzene, (L,D)-10-camphor-, ethylbenzene-,  
O-anisidine-5-, p-chlorobenzene-, hydroxybenzene-,  
20 trichlorobenzene-, 2-hydroxy-4-methoxy-benzophenone-, 4-nitrotoluene-2-, dinonylnaphthalene-,  
4-morpholineethane-, and 2-  
{[tris(hydroxymethyl)methyl]amino}-1-ethane-; and  
 $\text{C}_8\text{F}_{17}\text{COOH}$ , bis(2-ethyl hexyl hydrogen phosphate), and  
25 diphenyl hydrogen phosphate, which forms a complex with the polyaniline in an amount from 5 to 95 weight percent, having a conductivity equal or greater than about  $10^{-8}$  S-cm.

30           17. The conductive polymeric composition of claim 14 comprising polyaniline plus dodecylbenzenesulfonic acid which forms a complex with the polyaniline in an amount of from 5 to 95 weight

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perc nt, having a conductivity equal to or greater than about  $10^{-8}$  S-cm $^{-1}$ .

18. The conductive polymeric composition of  
5 claim 2 comprising a plasticizer selected from the group  
consisting of 4-hexyloxyphenol, 3-pentadecylphenol,  
nonylphenol, 4-dodecylresorcinol, 4-(tert-octyl)phenol,  
2,6-di-tert-butyl-4-methylphenol, 3,4-dimethylphenol,  
2,6-dimethylphenol, methyl p-toluenesulfonate, ethyl p-  
10 toluenesulfonate, n-hexyl p-toluenesulfonate,  
ethyldodecylbenzenesulfonic acid isopropylamine alkylaryl  
sulfonate, 1-dodecanol, 1-tridecanol, 1-docosanol,  
ethoxylates of the chemical formula  
 $\text{CH}_3(\text{CH}_2)_x\text{CH}_2(\text{OCH}_2\text{CH}_2)_n\text{OH}$ , where  $x=10-14$ ,  $n=1.3$ ;  $x=6.8$ ,  
15  $n=1.0$ ;  $x=10-12$ ,  $n=3$ ;  $x=6-8$ ,  $n=2$ ; poly(oxy-1,2-  
ethanediyl), alpha(nonylphenoxy)- $\omega$ -hydroxy and sulfated  
alkyl alcohol ethoxylate ammonium salt.

19. The conductive polymeric composition of  
20 claim 2 being a processible liquid and wherein the  
substrate comprises dissolved, molten or liquid bulk  
polymer or prepolymer.

20. The processible liquid conductive  
25 polymeric composition of claim 19 wherein the substrate  
additionally comprises a liquid solvent and/or a  
plasticizer.

21. The processible liquid conductive  
30 polymeric composition of claim 20 wherein said solvent is  
an organic solvent.

22. The processible liquid conductive  
polymeric composition of claim 21 wherein said solvent's  
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dielectric constant is smaller than about 22 and wherein said solvent is selected from the group consisting of alkanes and alkenes having from about 5 to about 12 carbon atoms, mineral oil, aromatics, halogenated aromatics, halogenated alkanes, and aliphatic alcohols, alkyl ethers and ketones having from 4 to about 12 carbon atoms, cycloalkanes, cycloalkenes, carbon tetrachloride, carbon disulfide, chloroform, bromoform, dichloromethane, morpholine, aniline, alkylbenzenes, xylene, toluene, decahydronaphthalene, styrene, benzyl alcohol, naphthalene, phenols, and cresols.

23. The processible liquid conductive polymeric composition of claim 20 wherein said plasticizer is selected from the group consisting of 4-hexyloxyphenol, 3-pentadecylphenol, nonylphenol, 4-dodecylresorcinol, 4-(tert-octyl)phenol, 2,6-di-tert-butyl-4-methylphenol, 3,4-dimethylphenol, 2,6-dimethylphenol, methyl p-toluenesulfonate, ethyl p-toluenesulfonate, n-hexyl p-toluenesulfonate, ethyldodecylbenzenesulfonic acid isopropylamine alkylaryl sulfonate, 1-dodecanol, 1-tridecanol, 1-docosanol, ethoxylates of the chemical formula  $\text{CH}_3(\text{CH}_2)_x\text{CH}_2(\text{OCH}_2\text{CH}_2)_n\text{OH}$ , where  $x=10-14$ ,  $n=1.3$ ;  $x=6.8$ ,  $n=1.0$ ;  $x=10-12$ ,  $n=3$ ;  $x=6-8$ ,  $n=2$ ; poly(oxy-1,2-ethanediyl), alpha(nonylphenoxy)- $\omega$ -hydroxy and sulfated alkyl alcohol ethoxylate ammonium salt.

24. The conductive polymeric composition of claim 5 wherein said polymer is selected from the group comprising polyethylenes, isotactic polypropylene, polystyrene, poly(ethylvinylacetate), polybutadiene, polyisoprene, ethylene-vinylene copolymers, poly(vinylchloride), ethylene-propylene copolymers,

polysiloxane, polysulfone, polycarbonates,  
poly(ethyleneterephthalate), homo- and copolymers of  
acrylonitrile, poly(butyleneterephthalate), nylon 12,  
nylon 8, nylon 6, nylon 6.6, nylon 4.6, amorphous nylons,  
5 poly(vinylacetate), poly(vinylbutyral) and poly(vinyl  
pyrrolidone).

25. The processible liquid conductive  
polymeric composition of claim 19 said composition being  
10 solidifiable into a transparent conductor having a  
conductivity greater than about  $10^{-8}$  S-cm<sup>-1</sup>, a surface  
resistance of less than  $10^6$  ohms/square and an integrated  
transmittance of more than 60% over the spectral range of  
485 to 675 nm.

15

26. The processible liquid conductive  
polymeric composition of claim 25 wherein the substrate  
comprises molten or liquid bulk polymer.

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27. The processible liquid conductive  
polymeric composition of claim 25 wherein the substrate  
comprises a liquid solvent and/or a plasticizer.

25

28. The processible liquid conductive  
polymeric composition of claim 25 wherein the substrate  
comprises solvent plus molten or liquid bulk polymer.

30

29. The processible liquid conductive  
polymeric composition of claim 28 wherein said substrate  
has a dielectric constant smaller than about 22 and said  
solvent is selected from the group consisting of alkanes  
and alkenes having from about 5 to about 12 carbon atoms,  
mineral oil, aromatics, halogenated aromatics,  
halogenated alkanes, and aliphatic alcohols, alkyl ethers

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and ketones having from 4 to about 12 carbon atoms, cycloalkanes, cycloalkenes, carbon tetrachloride, carbon disulfide, chloroform, bromoform, dichloromethane, morpholine, aniline, alkylbenzenes, xylene, toluene, 5 decahydronaphthalene, styrene, naphthalene, phenols, cresols, benzyl alcohol, epoxies, and acrylates.

30. The processible liquid conductive polymeric composition of claim 25 wherein the 10 functionalized protonic acid is a liquid having a dielectric constant equal to or smaller than about 22 and wherein said protonic acid serves as substrate as well.

31. A conductive polymeric material of claims 15 1-18 comprising polyaniline and a functionalized protonic acid, which forms a complex with the polyaniline, having a conductivity equal to or greater than about  $10^{-6}$  S-cm<sup>-1</sup> and an integrated transmittance of more than 60% over the spectral range of from 485 to 675 nm.

20 32. A conductive polymeric composition of claim 1 being a transparent conductor formed from a fluid polymeric composition comprising a substrate selected from organic solvents, molten polymers and oligomers 25 having a conductivity of less than  $10^{-8}$  S-cm<sup>-2</sup> and a dielectric constant at room temperature of 22 or less and having intimately admixed therewith polyaniline of film-forming molecular weight in admixture with an effective protonating amount of a protonic acid, the counter-ion of 30 said protonic acid being functionalized so as to be compatible with the substrate and forming a complex with the polyaniline and imparting a conductivity to the conductor greater than about  $10^{-8}$  S-cm<sup>-1</sup>, said conductor having a surface resistance of less than  $10^6$  ohms/square

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and an integrated transmittance of more than 60% over the spectral range of from 485 to 675 nm.

33. A transparent conductor according to claim  
5 32 said conductor has a surface resistance of less than  
1000 ohm/square and transmittance of more than 90 % in  
the spectral range from 475 to 675 nm.

34. A transparent conductor according to claim  
10 33 having a conductivity of at least  $10 \text{ S-cm}^{-1}$  and  
comprising polyaniline and (L,D)-10-camphorsulfonic acid.

35. A method of forming a conductive polymeric  
article which comprises the steps of:

15 a. forming a solution comprising polyaniline,  
a substrate including an organic liquid solvent that has  
a dielectric constant below 22 and optionally a  
nonconductive, or semiconductive substrate polymer and a  
functionalized protonic acid compatible with said solvent  
20 and said optional polymer; and

b. removing all or a portion of said solvent  
from said solution after or concurrent with shaping the  
solution into the desired article.

25 36. A method of forming a conductive polymeric  
article which comprises the steps of:

a. forming a solution comprising polyaniline,  
a liquid substrate of organic liquid monomers that has a  
dielectric constant below 22 and a functionalized  
30 protonic acid compatible with said substrate; and

b. polymerizing the monomers in said solution,  
after or concurrent with shaping the solution into the  
desired article.

37. A method of forming a conductive polymeric article from a solution which compromises the steps of:

5 a. forming a solution comprising polyaniline, a solvent that has a dielectric constant below 22 and a functionalized protonic acid compatible with the solvent and substrate polymers and one or more bulk substrate polymers; and

10 b. removing all or a portion of said solvent from said solution, thereby giving rise to the conductive polymeric article.

38. A method of forming a solid conductive polymeric article having a nonconductive substrate polymer which compromises the steps of:

15 a. forming a solution comprising polyaniline, organic liquid monomer precursor to said substrate polymer, and a functionalized protonic acid solute compatible with said monomer; and

20 b. polymerizing the monomer to yield the solid article.

39. A method of forming a conductive article of conductive polyaniline with substrate by:

25 a. forming a melt comprising polyaniline, and a functionalized protonic acid solute intimately admixed in a molten polymer substrate selected from the group consisting of thermoplastic polymers; and

b. solidifying said melt.

30 40. A light-emitting diode comprising the transparent electrode of claims 31-34.

41. An electrically conductive article comprising the material of claims 1-18, 31-34, and 24

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selected from the group consisting of fibers, rods, profiles, films, coatings, membranes, containers, casings, and uses thereof.

5           42. An electrically conductive liquid comprising the material of claims 19-23 and 25-30 selected from the group consisting of glues, adhesives, inks, paints, sprays, oils, pastes and waxes, and uses thereof.

10

          43. A conductive polymeric composition according to claim 1 prepared by emulsion polymerization.

15           44. A flexible light-emitting diode comprising a conducting hole-injecting electrode comprising a conductive polymeric material of claim 31 and an electroluminescent layer comprising a flexible conjugated polymer.

20           45. The flexible light-emitting diode of claim 44 additionally comprising a electron-injecting contact having a work function below 4.3.

25           46. The flexible light-emitting diode of claim 45 additionally comprising a flexible polymer support in contact with the conducting hole-injecting electrode.

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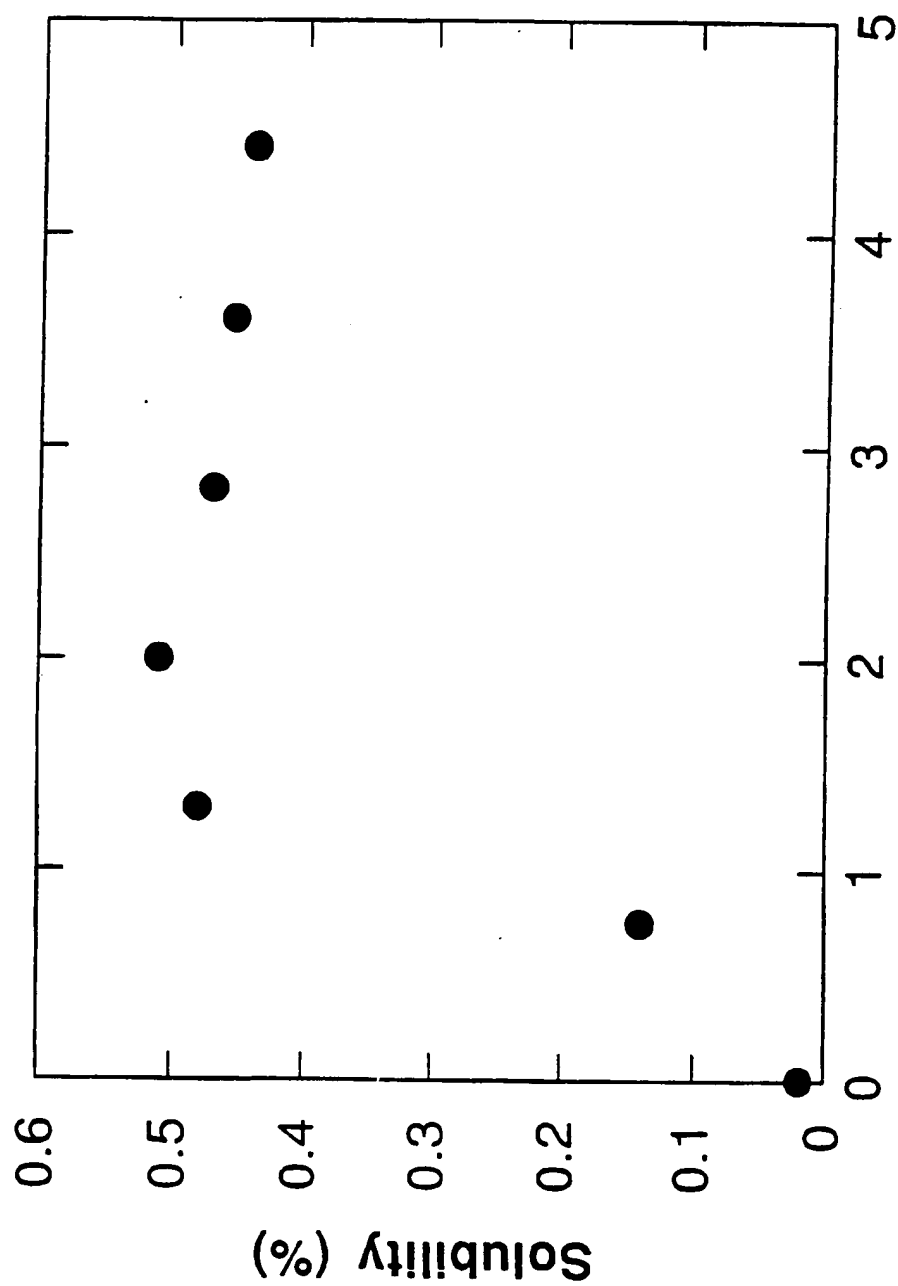
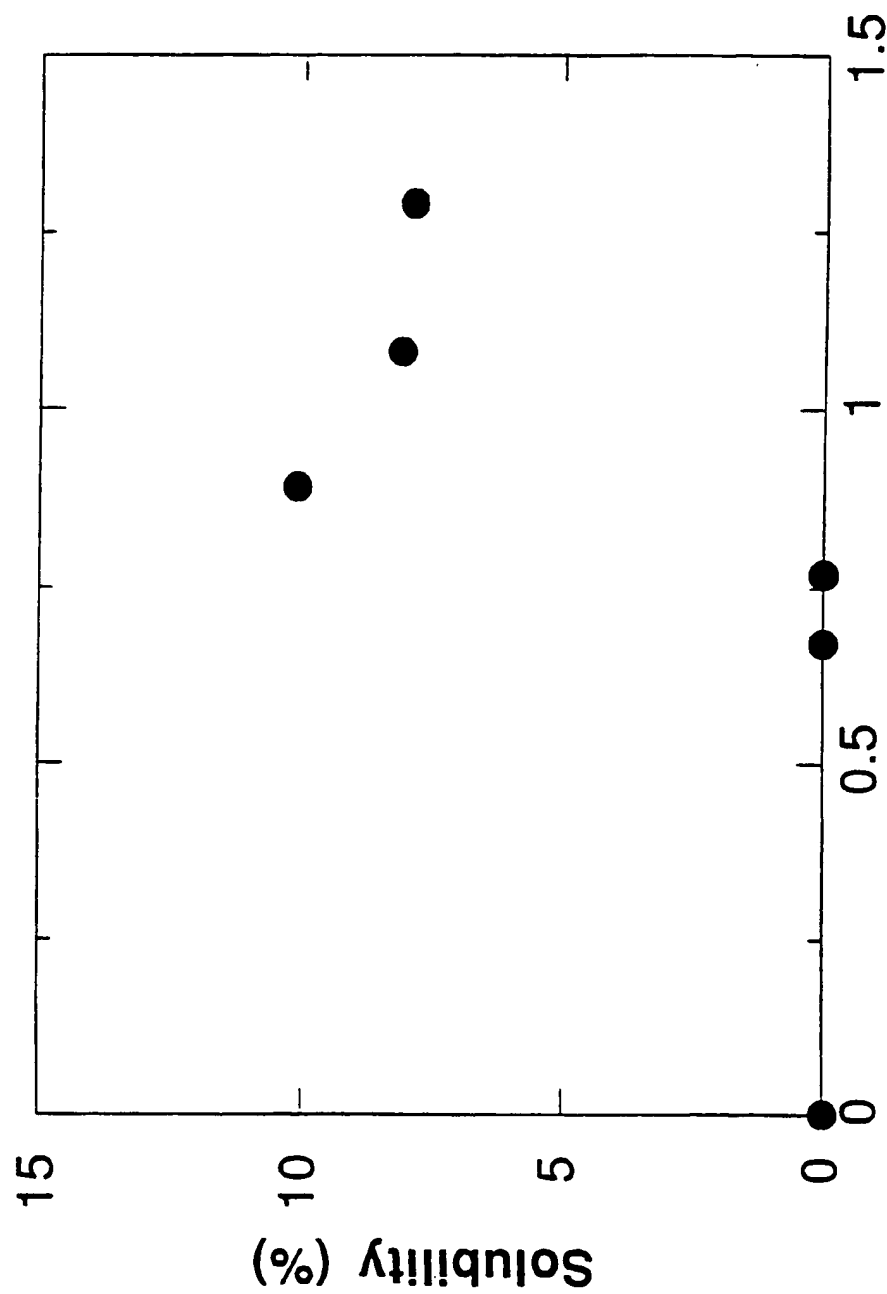


Fig. 1A DBSA/PhN molar ratio

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**Fig. 1B DBSA/PhN molar ratio**

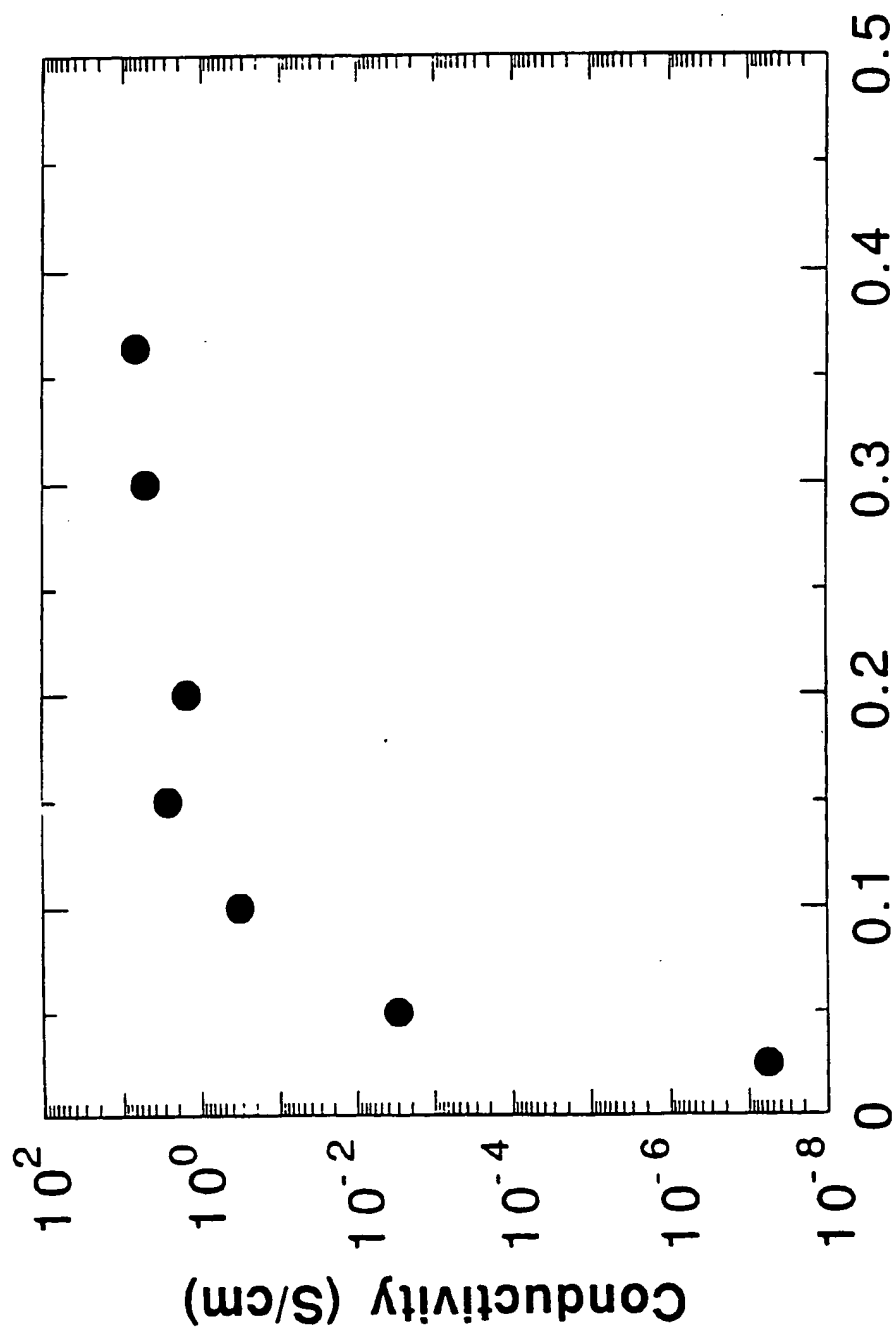


Fig. 2A PANI-DBSA fraction (w/w)

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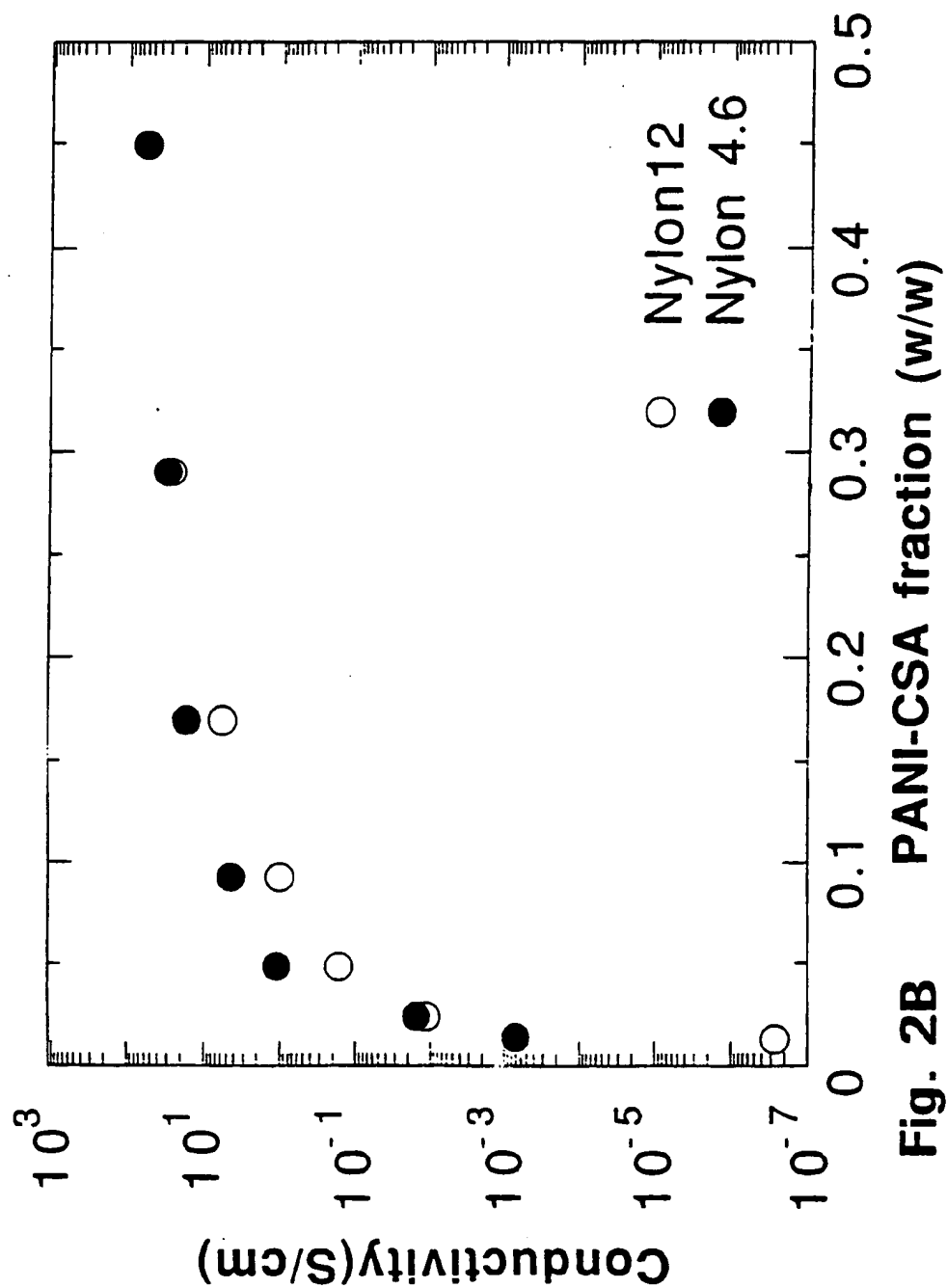


Fig. 2B PANI-CSA fraction (w/w)

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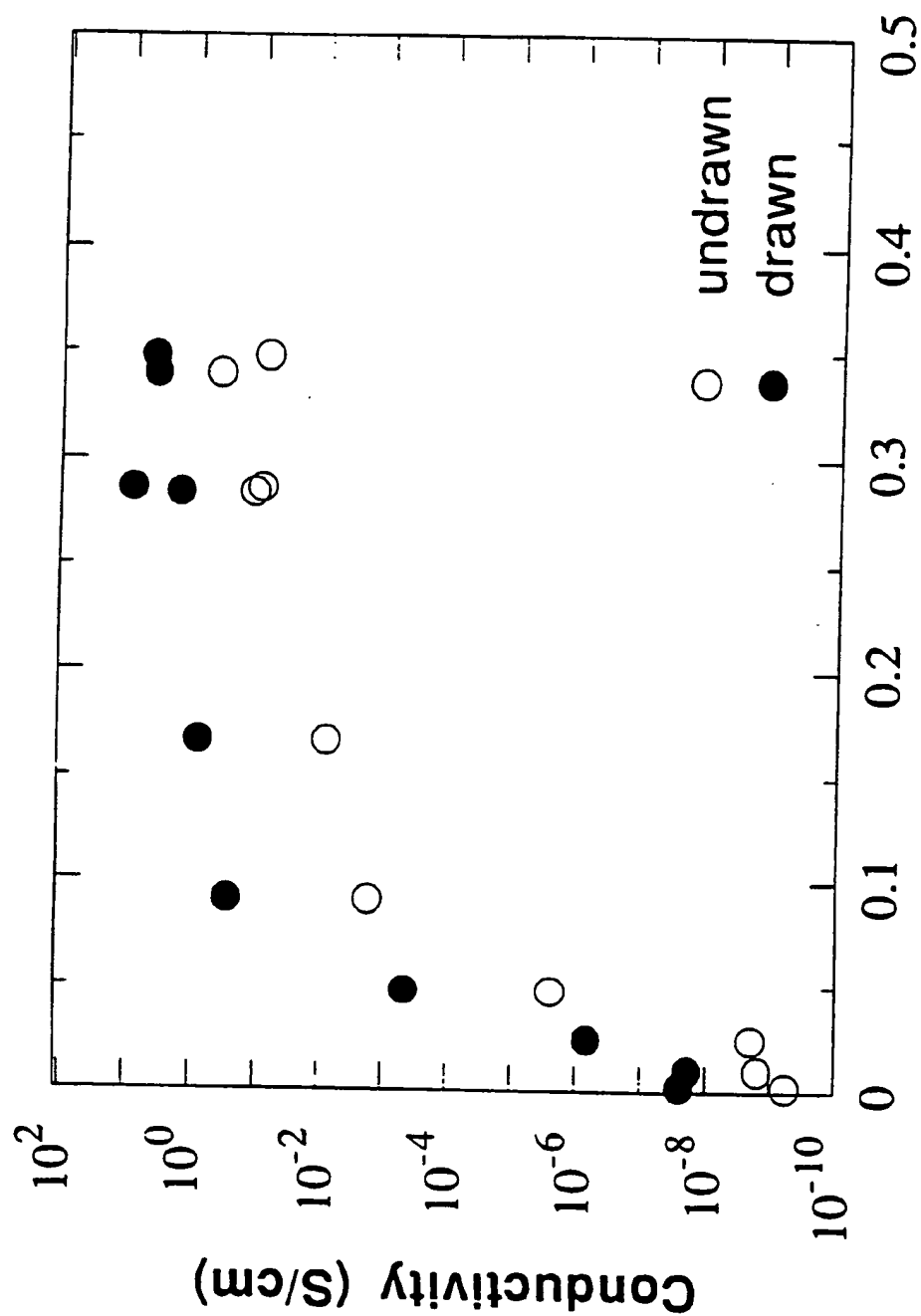
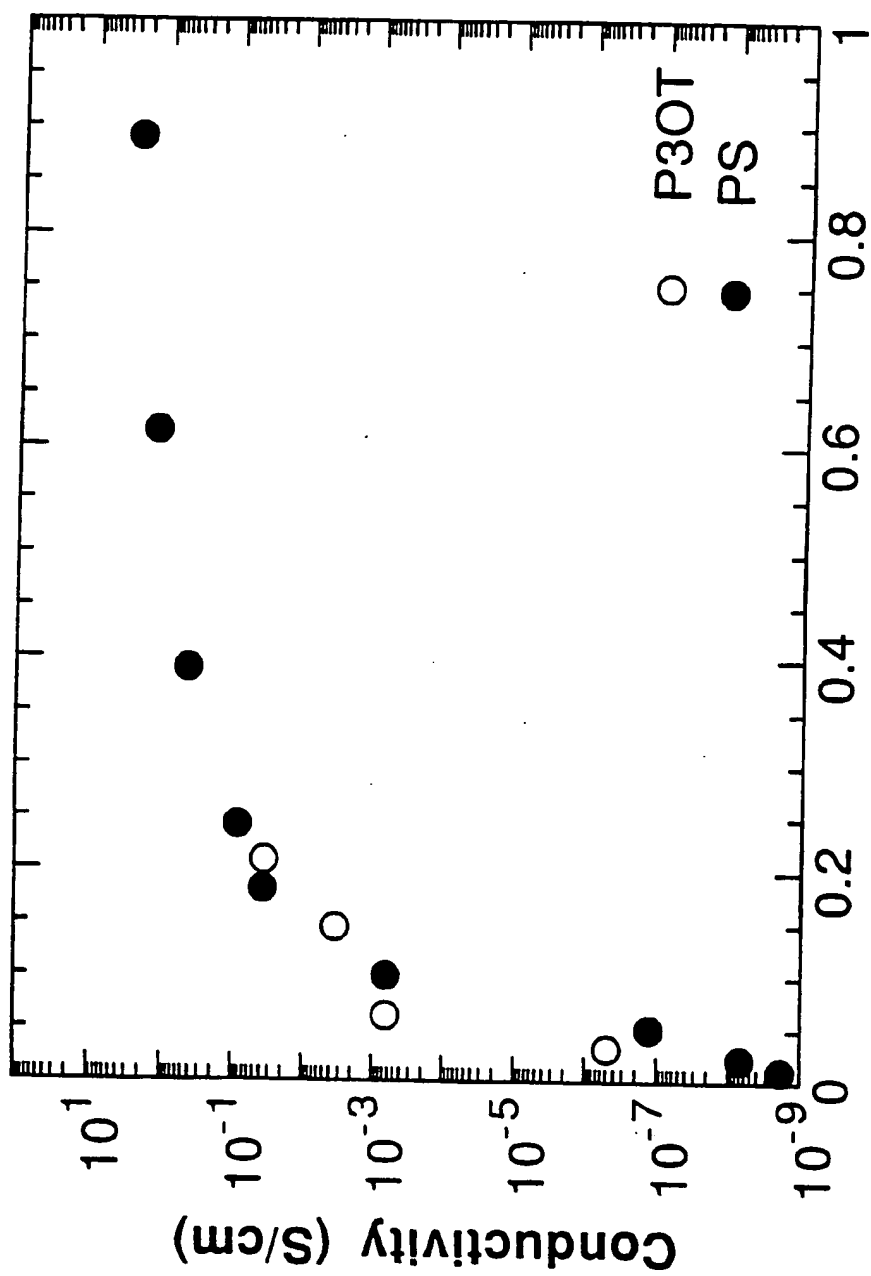


Fig. 3 PANI-DBSA fraction (w/w)

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**Fig. 4 PANI-DBSA fraction (w/w)**

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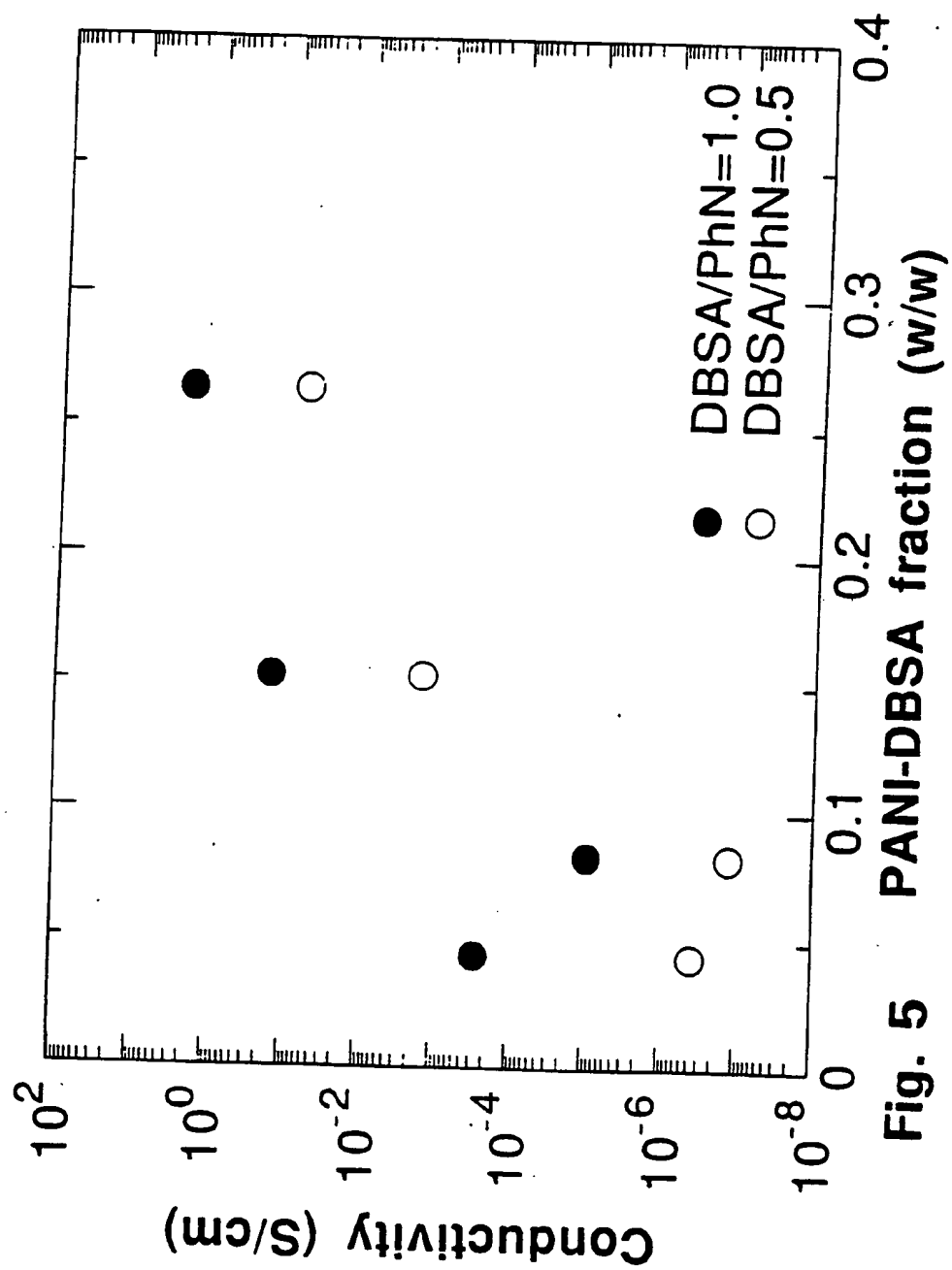
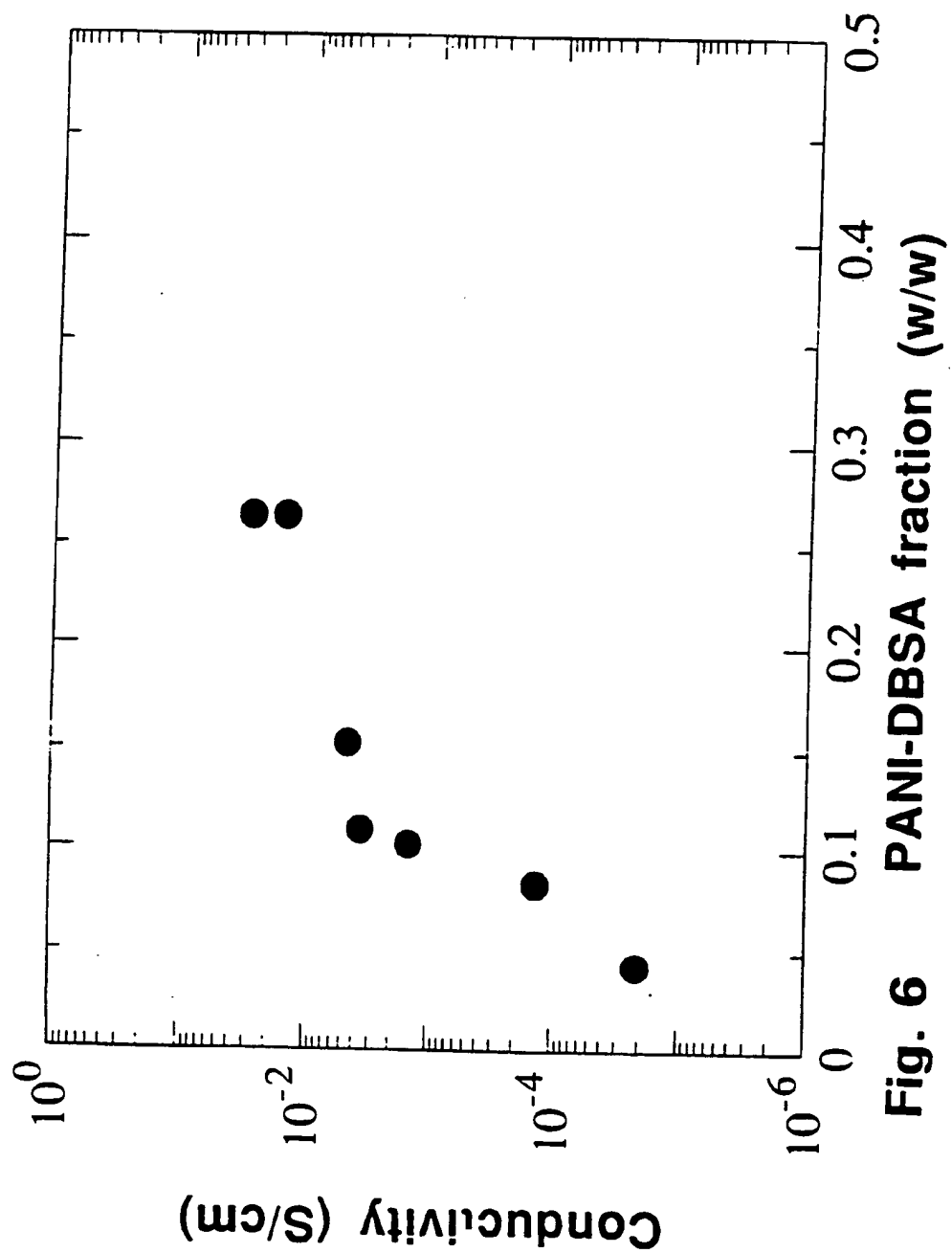


Fig. 5

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**Fig. 6 PANI-DBSA fraction (w/w)****SUBSTITUTE SHEET**

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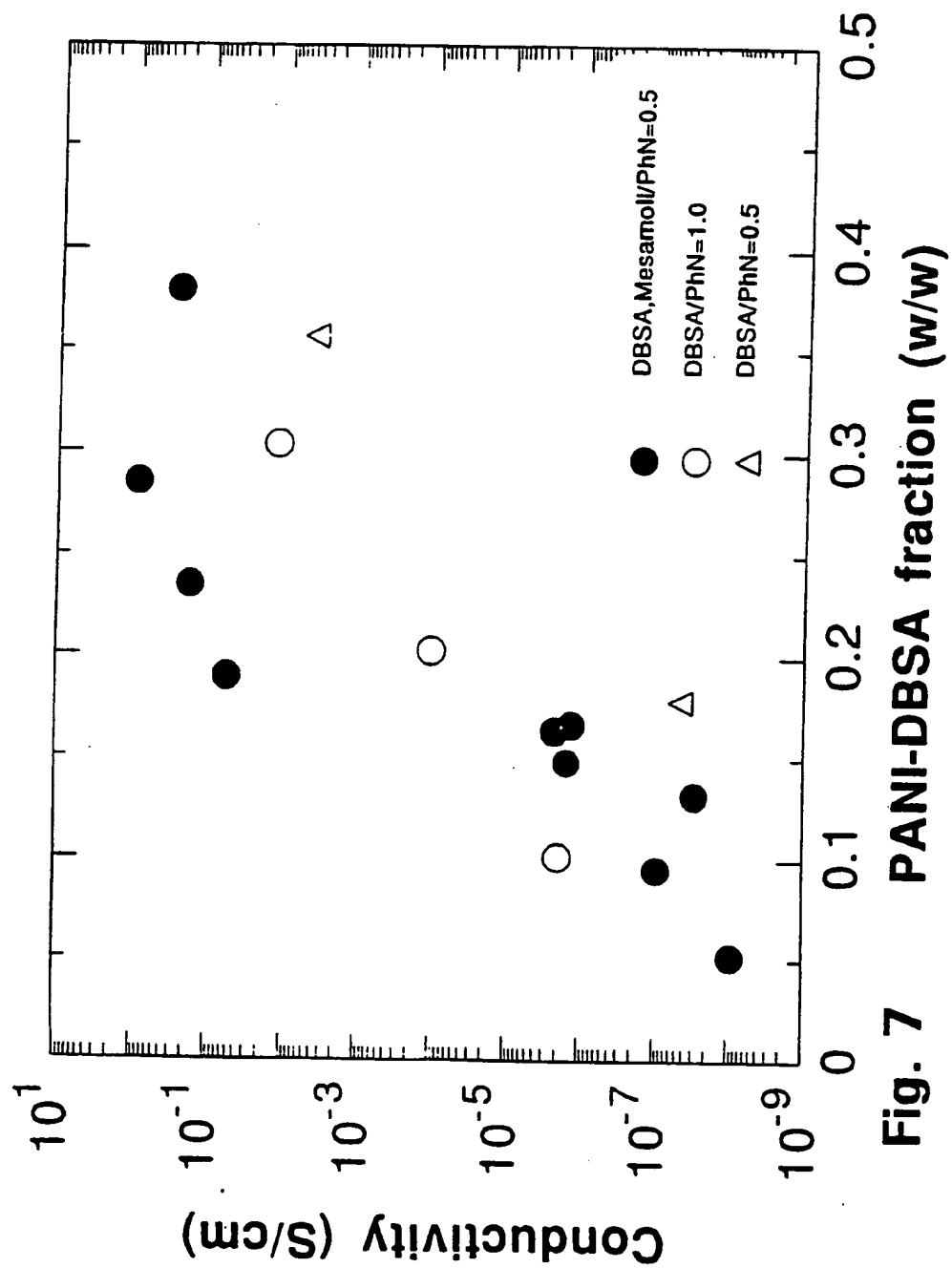


Fig. 7

PANI-DBSA fraction (w/w)

SUBSTITUTE SHEET

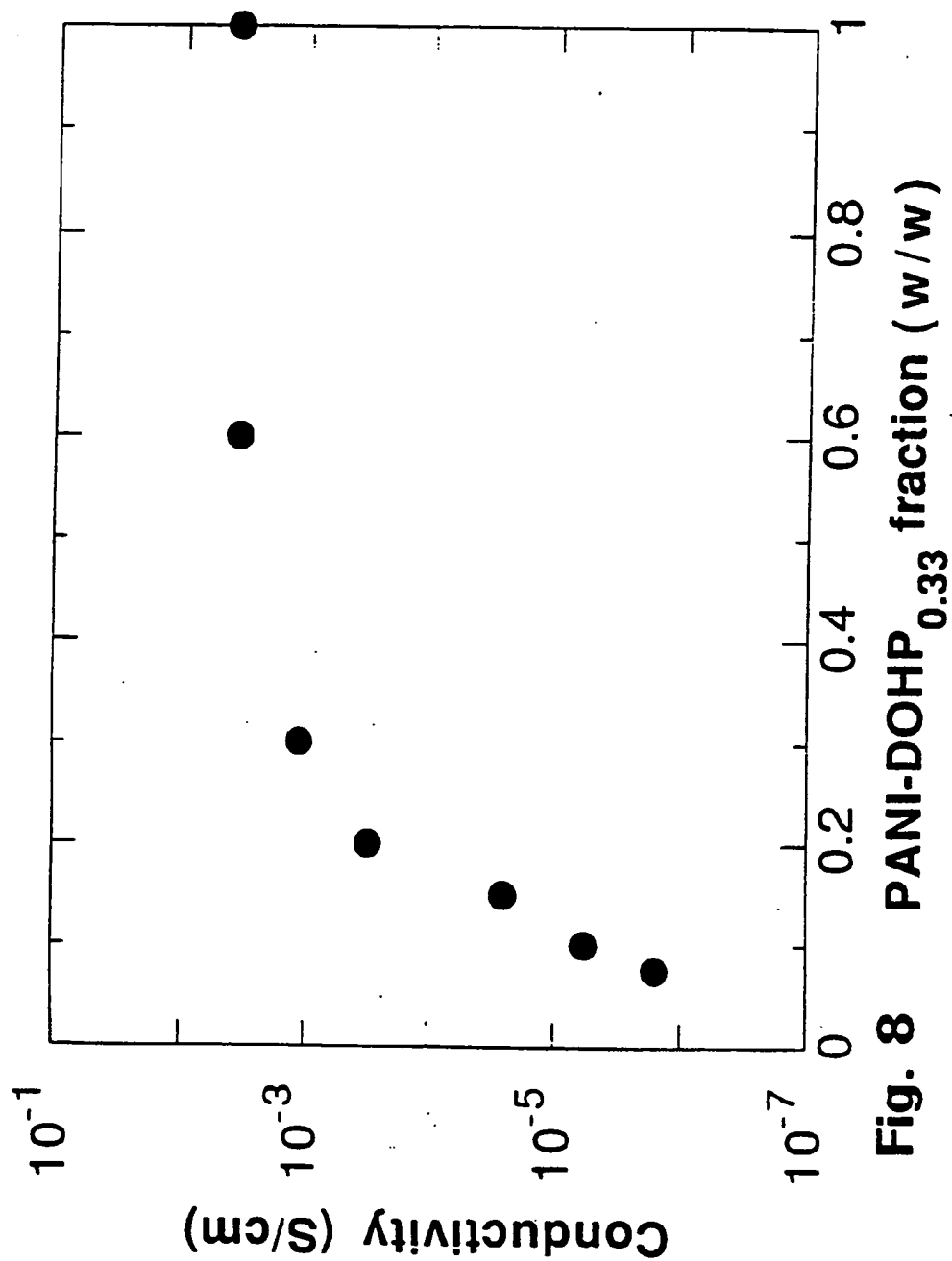


Fig. 8 PANI-DOHP<sub>0.33</sub> fraction (w/w)

SUBSTITUTE SHEET

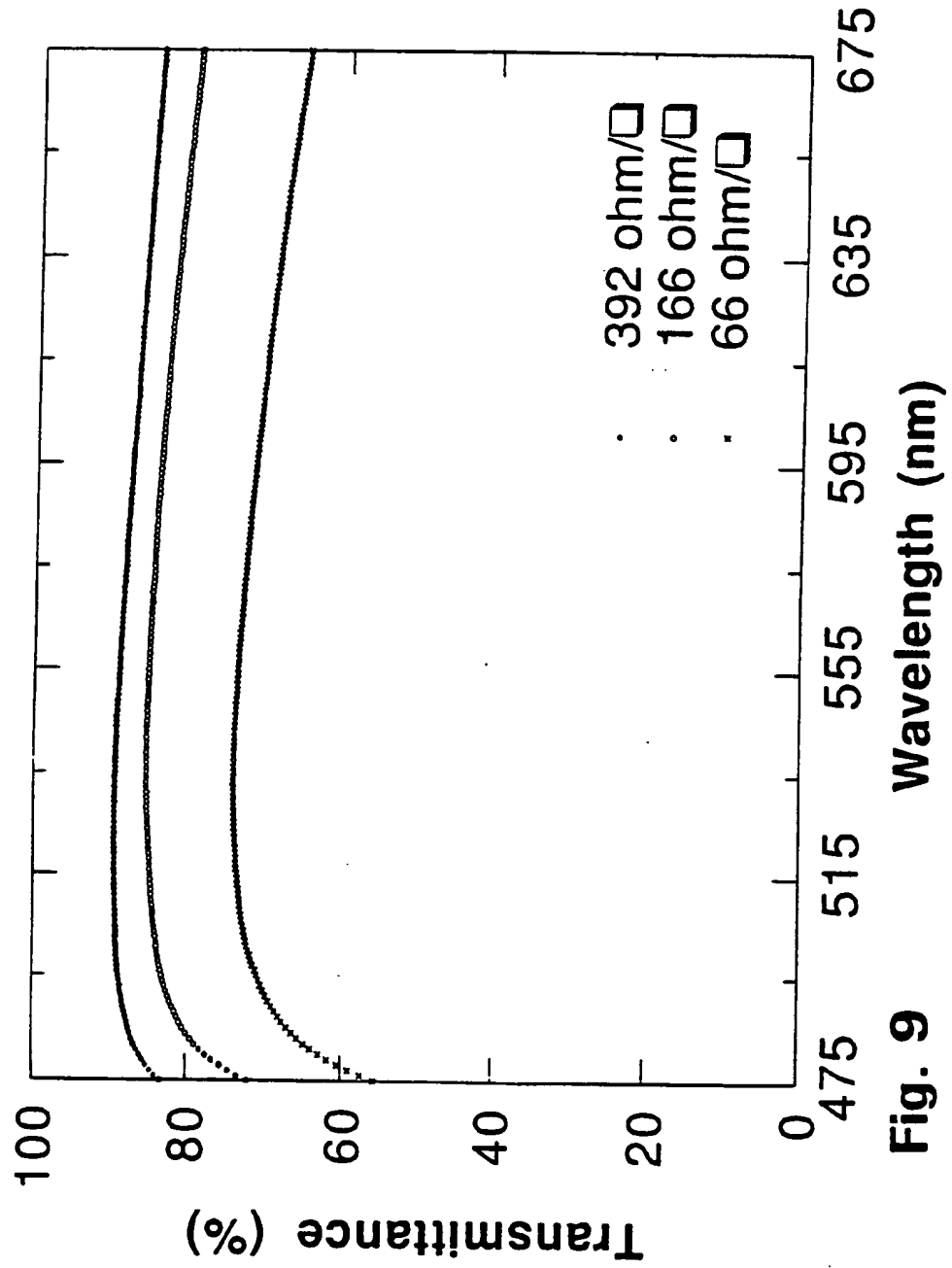


Fig. 9

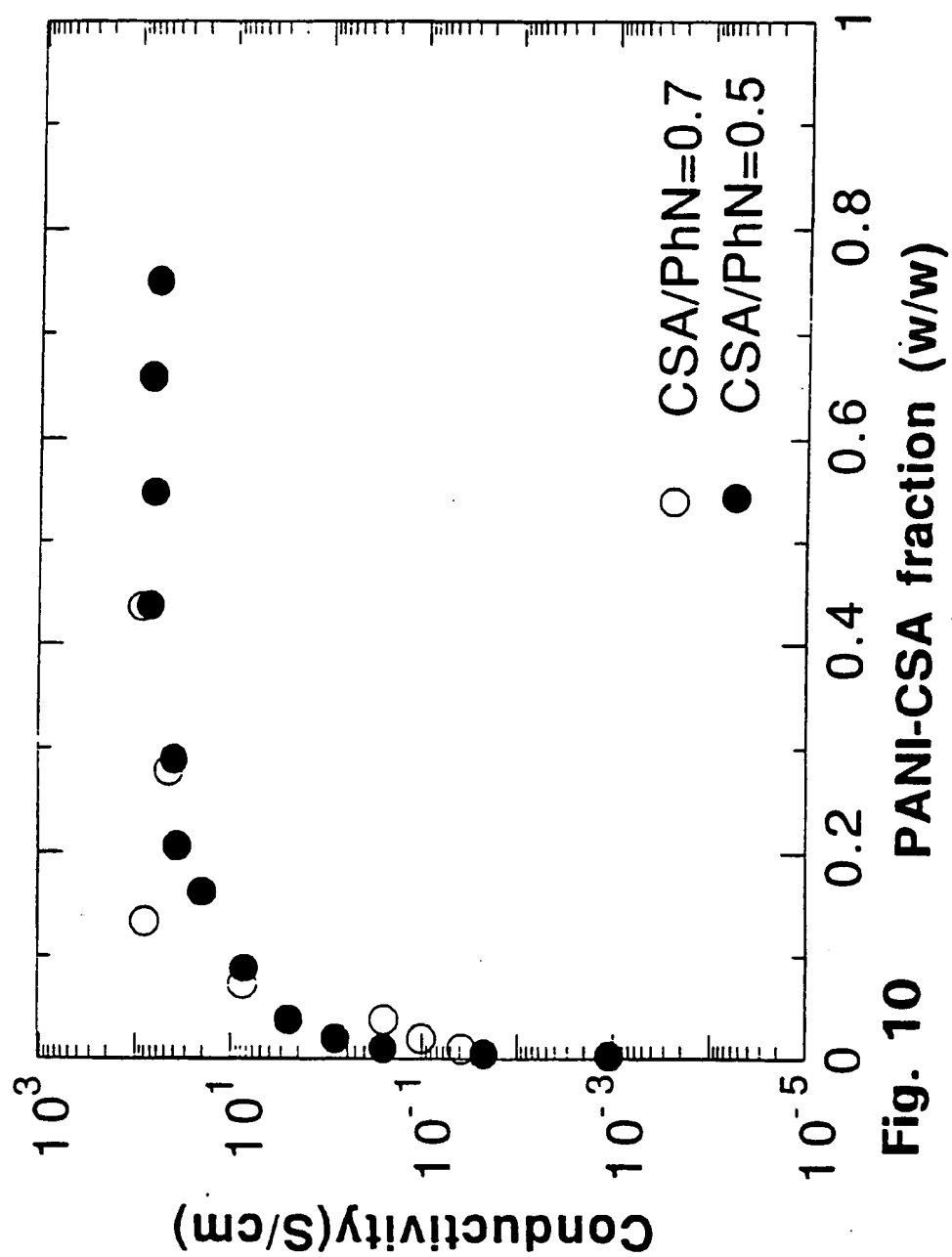


Fig. 10

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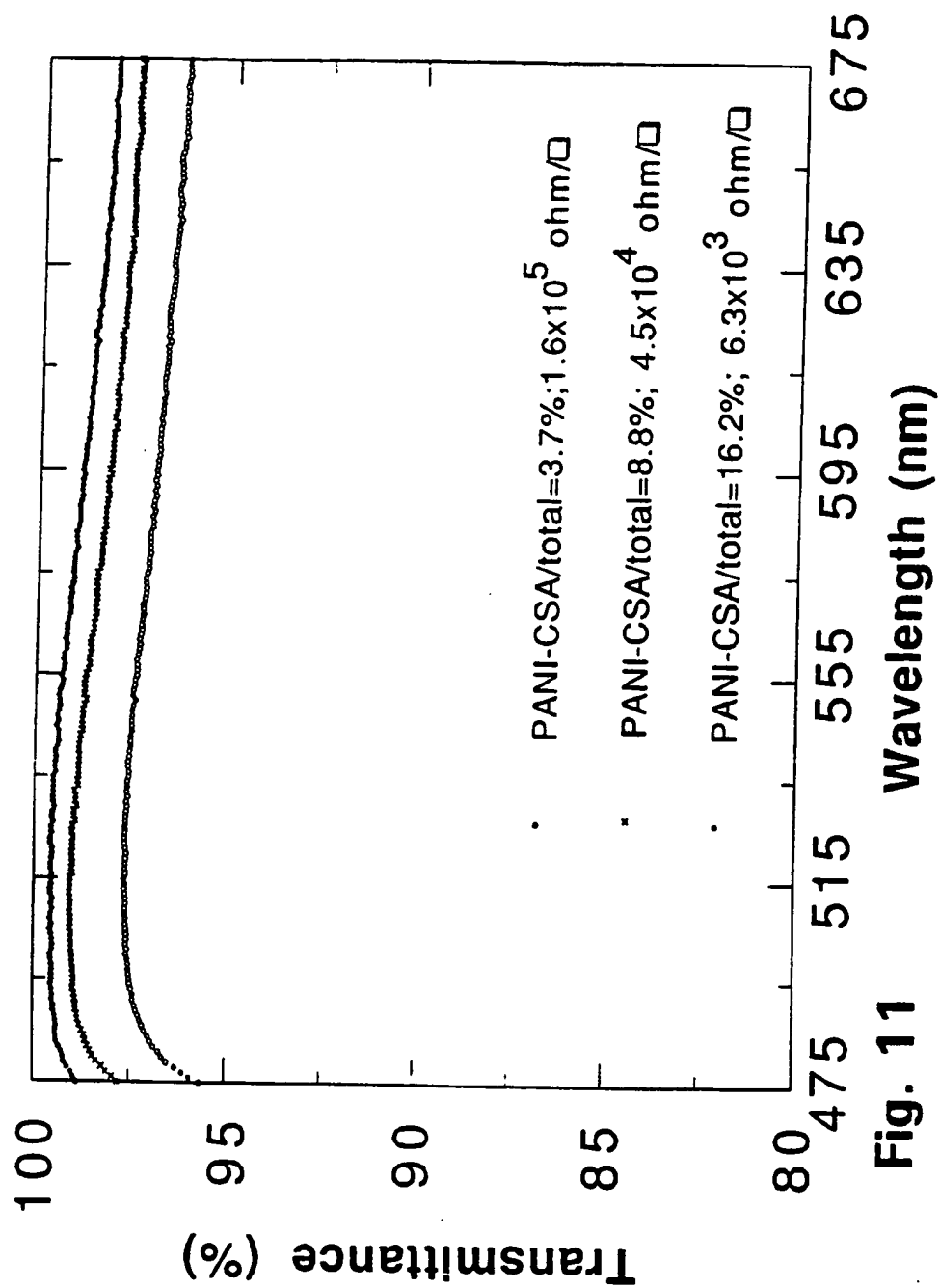


Fig. 11

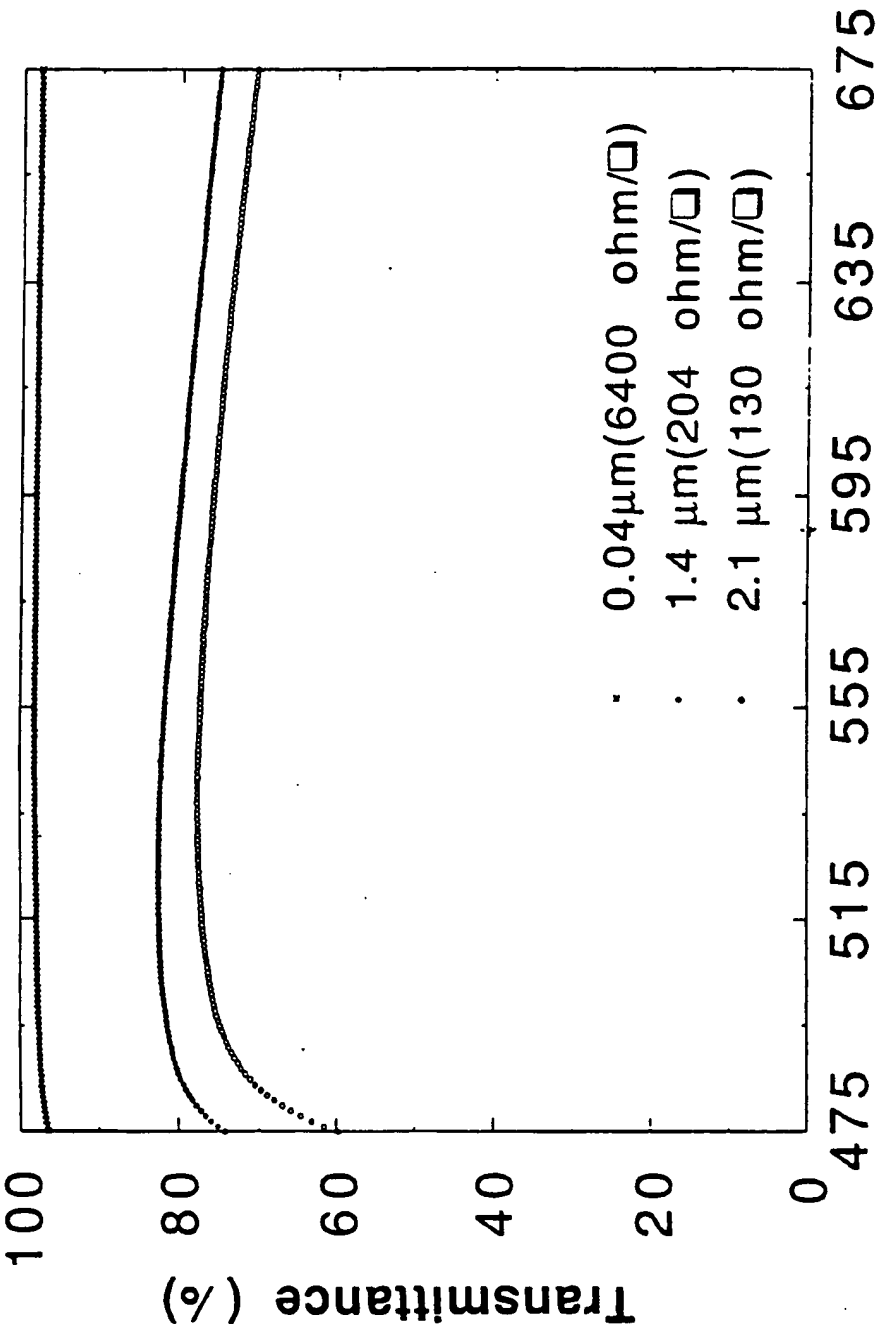


Fig. 12 Wavelength (nm)

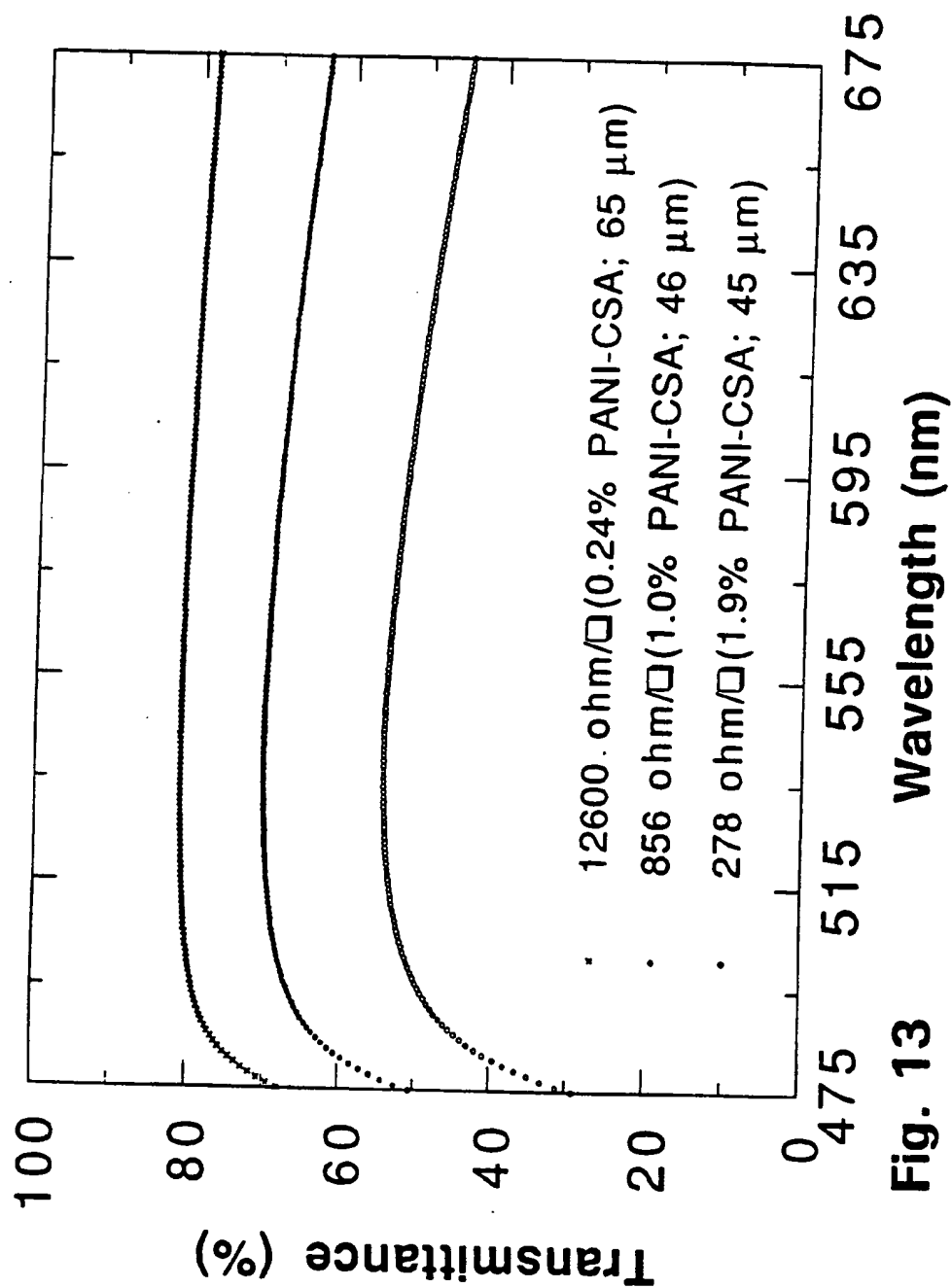
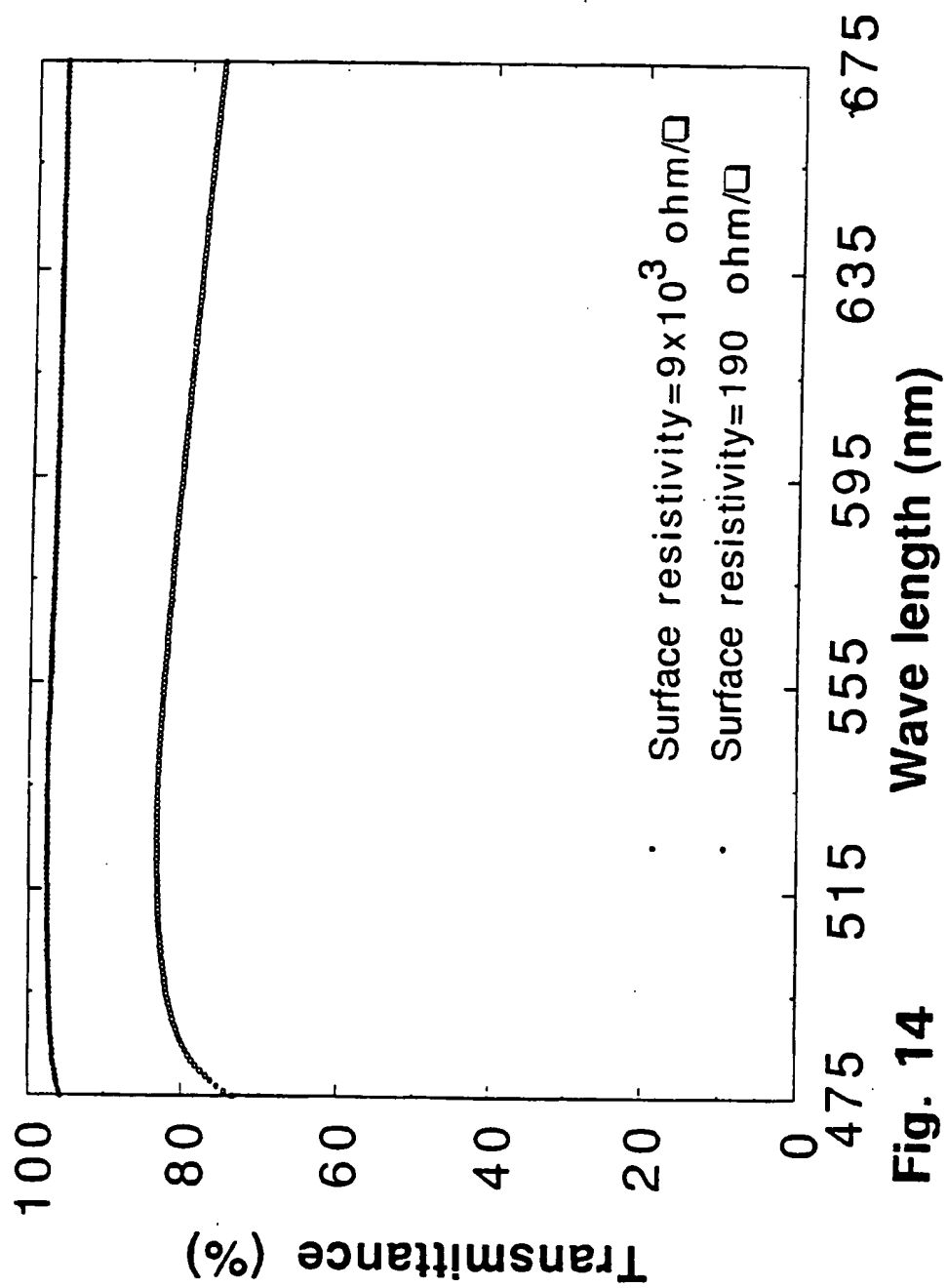


Fig. 13

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**Fig. 14**

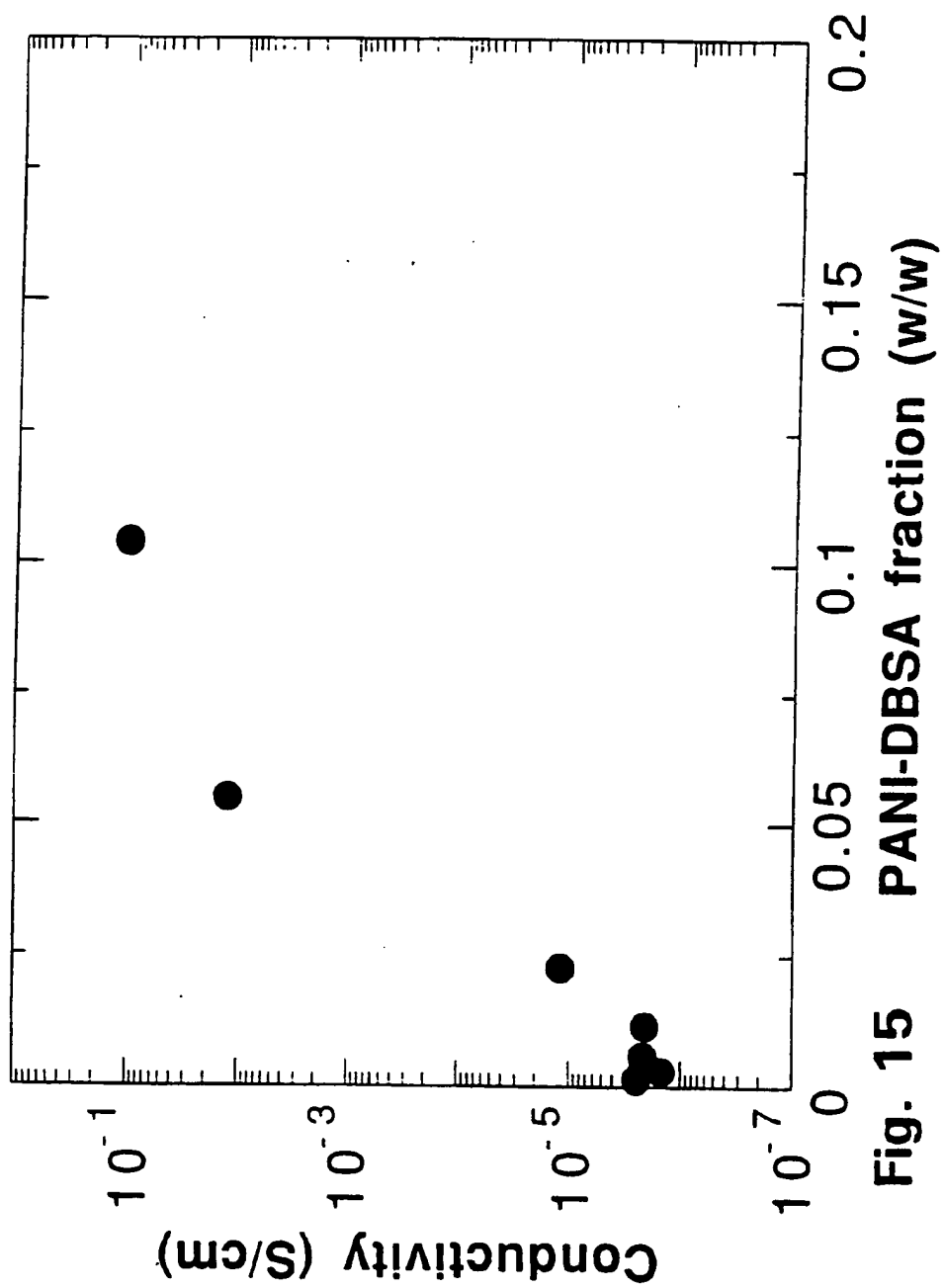


Fig. 15

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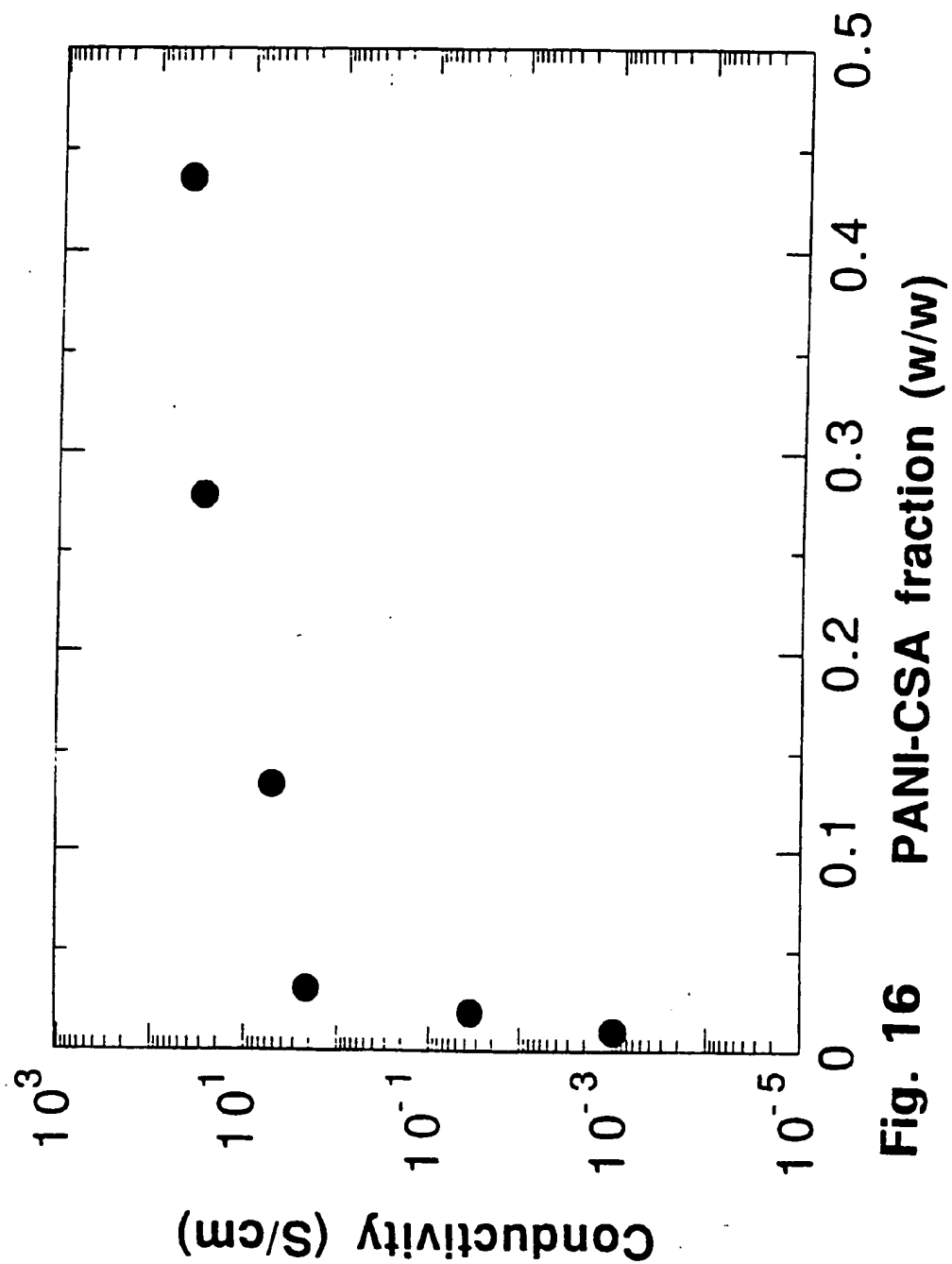


Fig. 16

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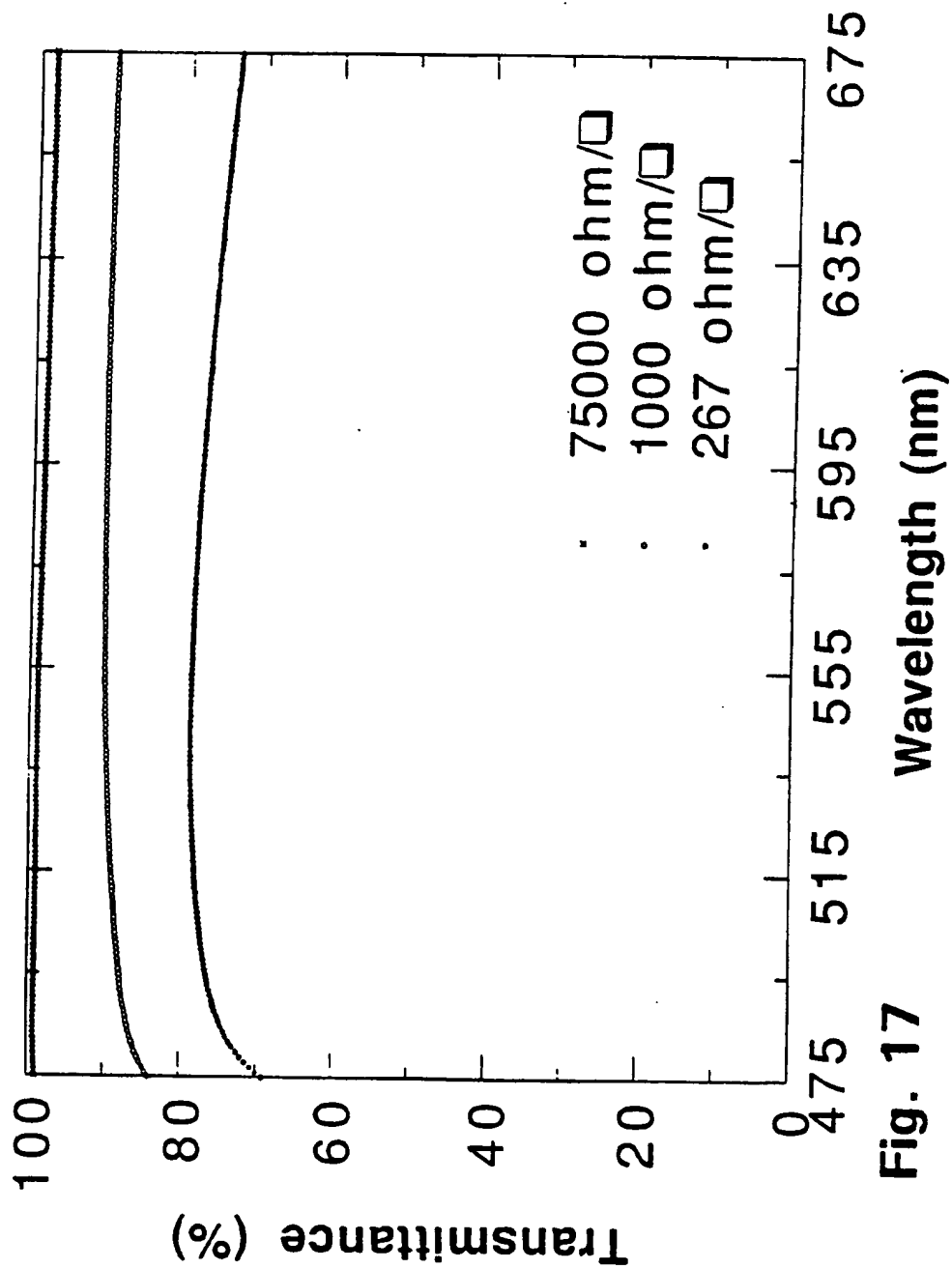
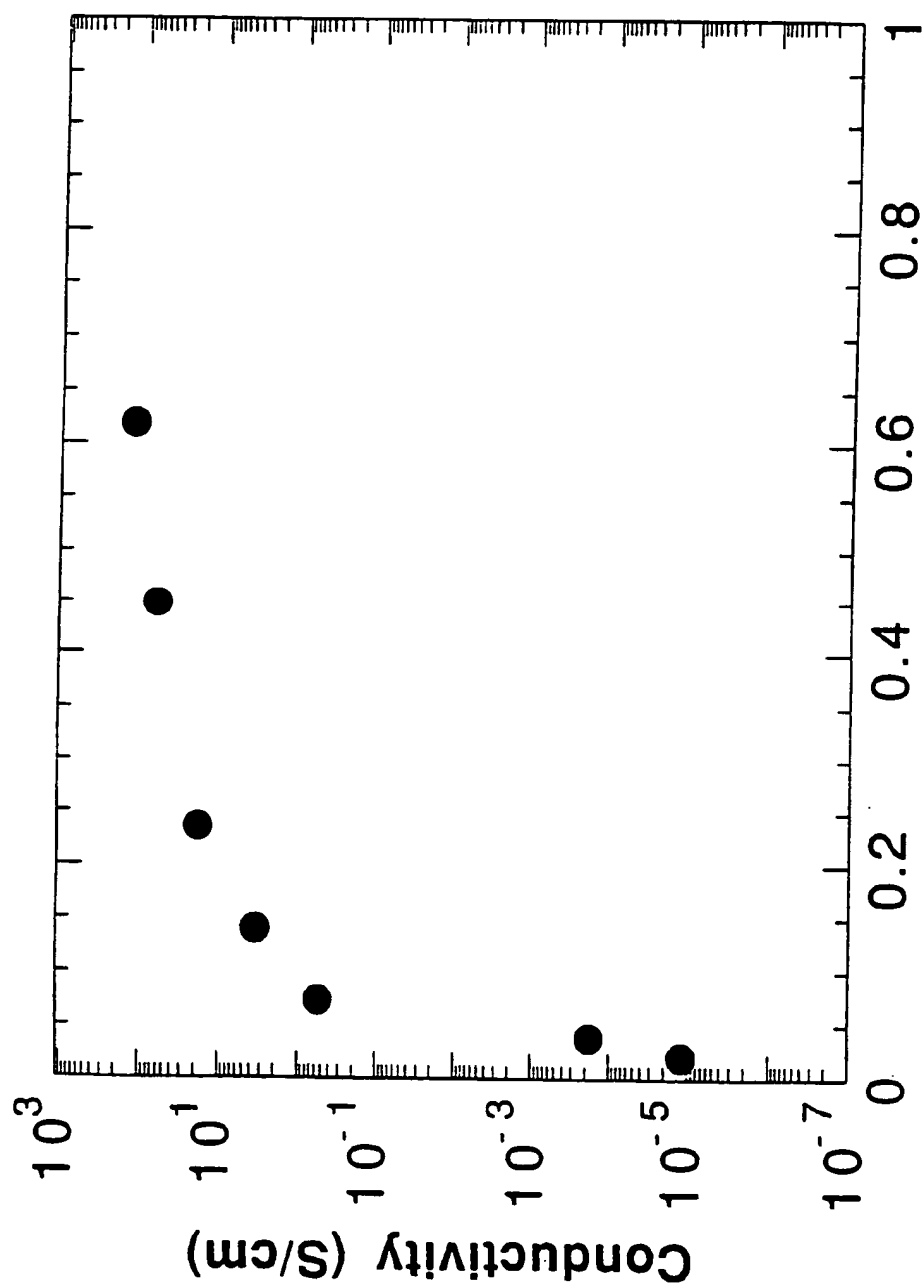


Fig. 17

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**Fig. 18** PANI-CSA fraction (w/w)

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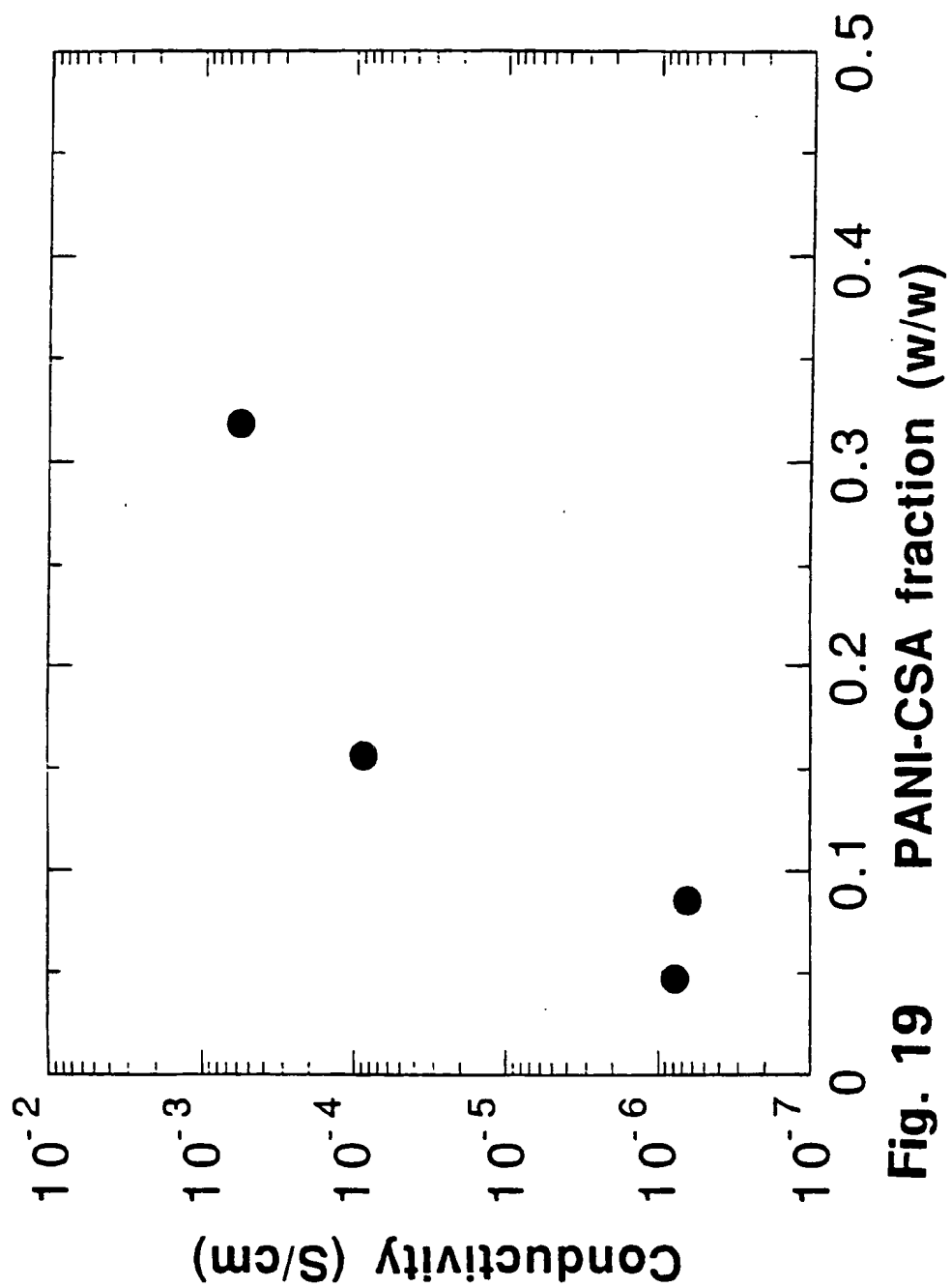


Fig. 19

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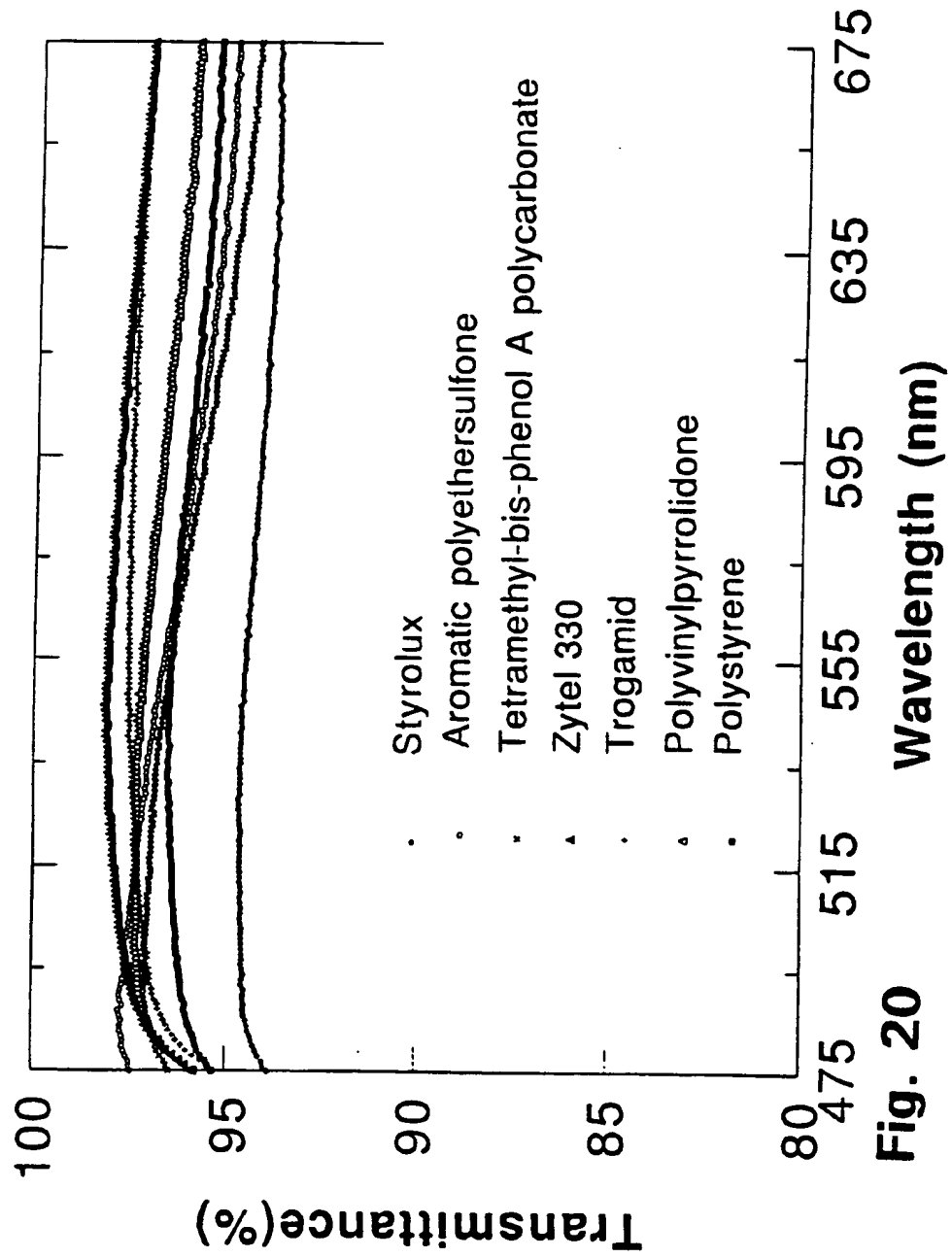


Fig. 20

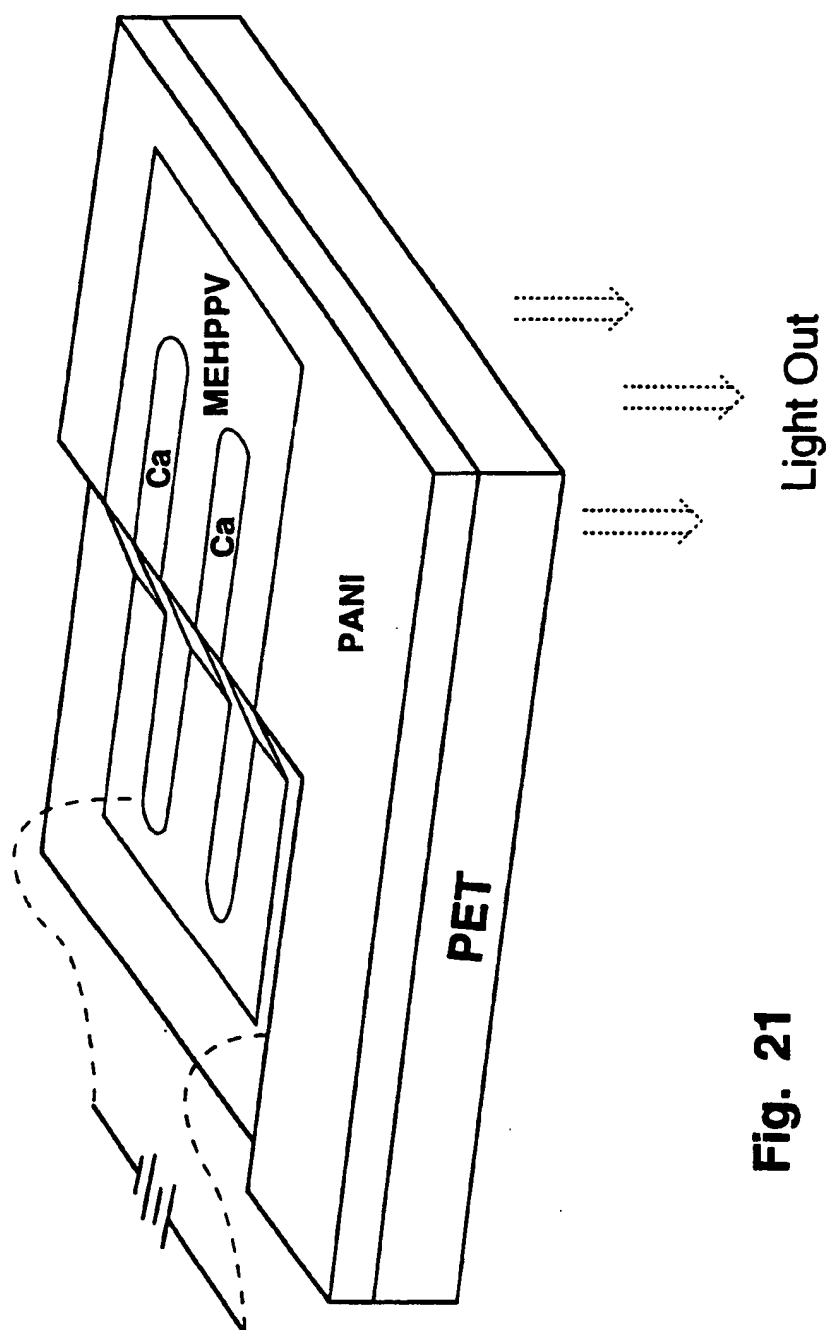
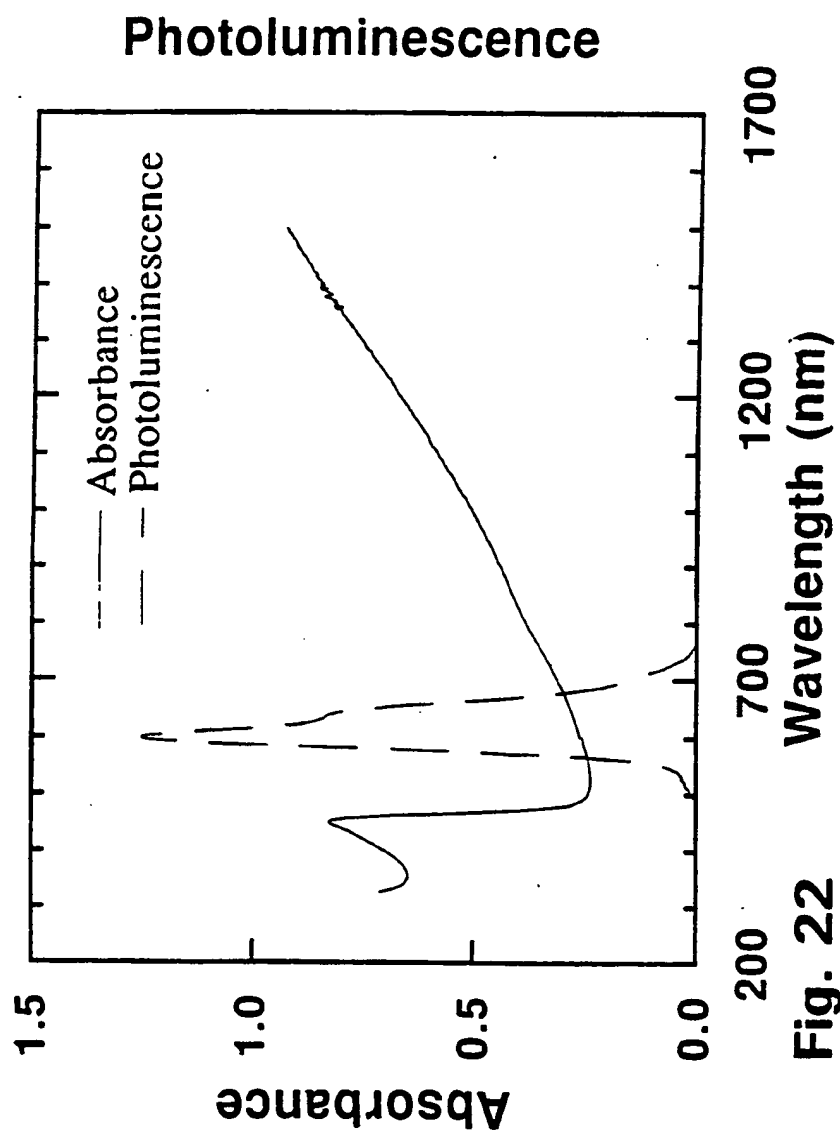


Fig. 21

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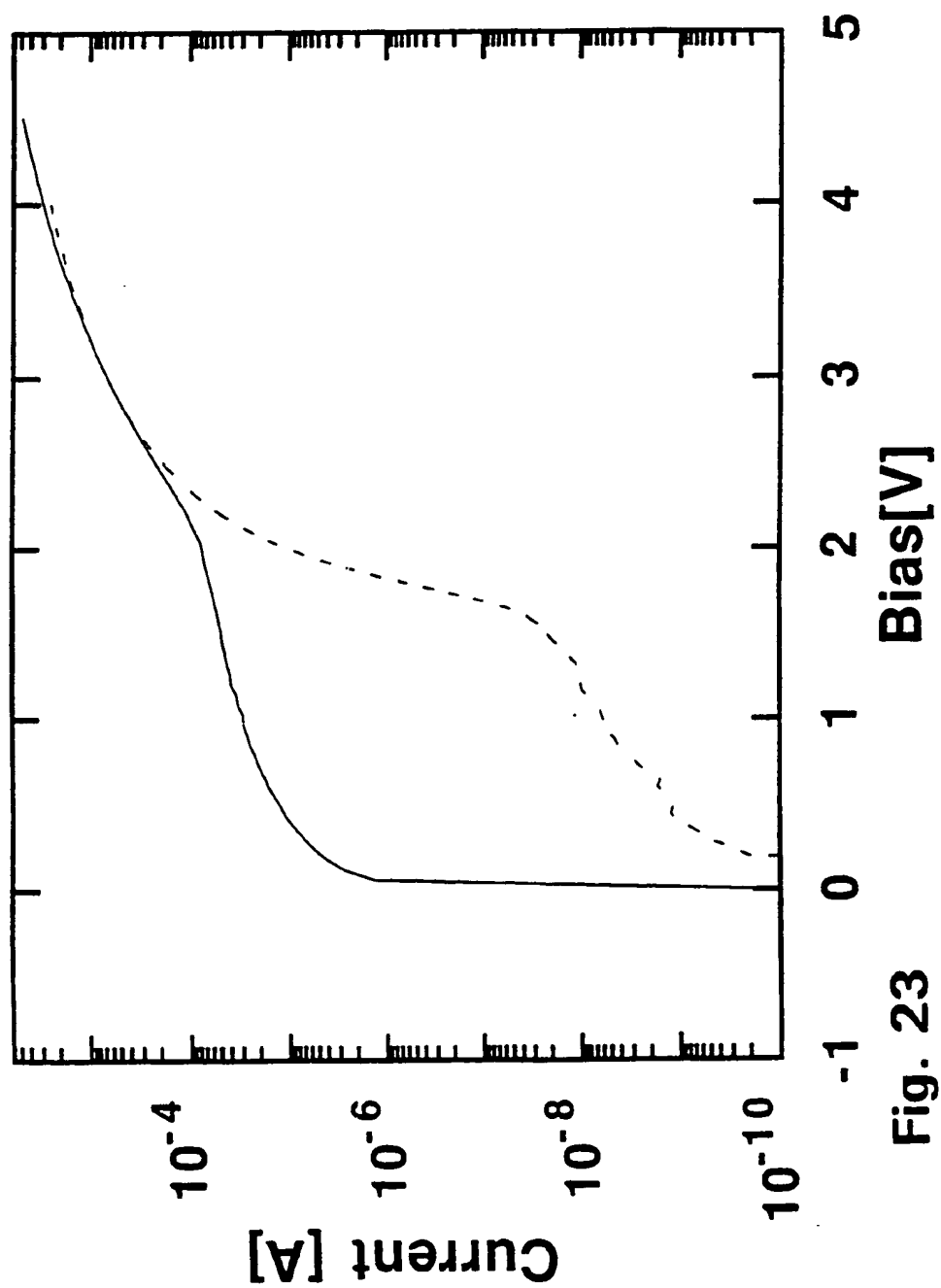


Fig. 23

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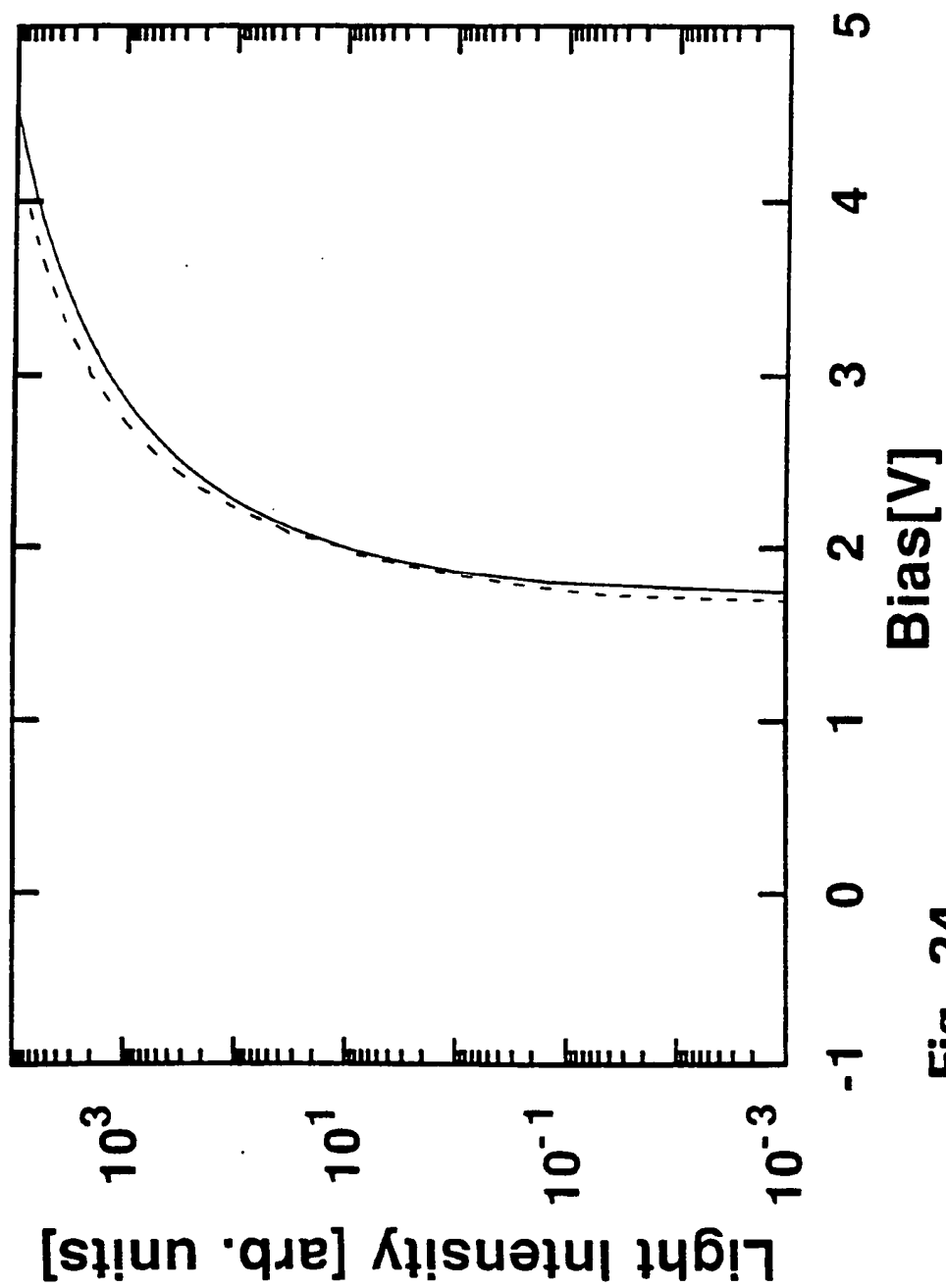


Fig. 24

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US92/04167

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(5) :H01B 1/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 252/500,518;  
525/540,528/422

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A, 4,851,487 (YANIGER et al) 25 July 1989 See column 1, lines 24-34	1-12 & 35-39
Y	US,A, 935,163 (CAMERON) 19 June 1990 See column 2, line 59 - Column 4, line 68	1-30, 32-39 & 43
Y,P	US,A, 5,093,439 (EPSTEIN ET AL)03 March 1992 See entire document	1-30, 32-39
Y,P	US,A, 5,079,096 (MIYAKE ET AL)07 January 1992 See columns 1-4	1-30, 32-39 & 43
Y	US,A, 5,008,041 (CAMERON ET AL) 16 April 1991 See column 3-4	1-30, 32-39 & 43
Y	JP,A, 2-240163, (TOMOEGAWA PAPER) 25 September 1990 See Abstract	1-16 & 35-39
E	US,A, 5,133,841 (HIGO ET AL) 28 July 1992 See Columns - 2	1-13, 35-39

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
*A* document defining the general state of the art which is not considered to be part of particular relevance	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
*E* earlier document published on or after the international filing date	*Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
*L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*G*	document member of the same patent family
*O* document referring to an oral disclosure, use, exhibition or other means		
*P* document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 18 AUGUST 1992	Date of mailing of the international search report 30 SEP 1992
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Washington, D.C. 20231

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Authorized officer

ANTHONY GREEN

Telephone No. (703) 308-3819

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US92/04167

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☒ Claims Nos.: 31, 40, 41, 42, 44, 45, 46  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐

The additional search fees were accompanied by the applicant's protest.

☐

No protest accompanied the payment of additional search fees.